



Isotope Geochemistry and Chronology of Offshore Ground Water Beneath Indian River Bay, Delaware

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
Volume		
liter (L)	0.2642	gallon
liter (L)	0.03531	cubic foot
Mass		
gram (g)	0.03527	ounce, avoirdupois
kilogram (kg)	2.205	pound, avoirdupois
Pressure		
kilopascal (kPa)	0.009869	atmosphere, standard
kilopascal (kPa)	0.01	bar
kilopascal (kPa)	0.2961	inch of mercury at 60 °F
Radioactivity		
tritium unit (TU)	0.118	becquerel per kg (Bq/kg) of water
tritium unit (TU)	3.19	picocurie per kg (pCi/kg) of water

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \cdot ^{\circ}\text{C}) + 32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929. Elevations are given in meters (or feet) above sea level.

ABBREVIATIONS AND ACRONYMS

km	kilometer
m	meter
cm	centimeter
μm	micrometer
ft	feet
kg	kilogram
g	gram
mg	milligram
L	liter
mL	milliliter
mmol	millimole
μmol	micromole
fmol	femtomole (10^{-15} mole)
mS/m	millisiemens per meter
μS/m	microsiemens per meter
ccSTP	cubic centimeters of dry gas at standard temperature (0 °C) and pressure (1 atmosphere)
‰	per mil (part per thousand)
pptv	parts per trillion by volume (atmospheric mixing ratio of gas in equilibrium with a water sample at sea level)
TU	tritium unit (1 atom of ^3H per 10^{18} atoms of ^1H)
LDEO	Lamont Doherty Earth Observatory (Noble Gas Laboratory)
MPTL	USGS Menlo Park Tritium Laboratory
NWQL	USGS National Water Quality Laboratory
RCFC	USGS Reston Chlorofluorocarbon Laboratory
RSIL	USGS Reston Stable Isotope Laboratory
RWCL	USGS Reston Water Chemistry Laboratory
UDEL	University of Delaware at Lewes
USGS	U.S. Geological Survey

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ABSTRACT

Results of geophysical surveys in Indian River Bay, Delaware, indicate a complex pattern of salinity variation in subestuarine ground water. Fresh ground-water plumes up to about 20 meters thick extending hundreds of meters offshore are interspersed with saline ground water, with varying degrees of mixing along the salinity boundaries. It is possible that these features represent pathways for nutrient transport and interaction with estuarine surface water, but the geophysical data do not indicate rates of movement or nutrient sources and reactions. In the current study, samples of subestuarine ground water from temporary wells with short screens placed 3 to 22 meters below the sediment-water interface were analyzed chemically and isotopically to determine the origins, ages, transport pathways, and nutrient contents of the fresh and saline components. Apparent ground-water ages determined from chlorofluorocarbons (CFCs), sulfur hexafluoride (SF₆), tritium (³H), and helium isotopes (³He and ⁴He) commonly were discordant, but nevertheless indicate that both fresh and saline ground waters ranged from a few years to at least 50 years in age. Tritium-helium (³H-³He) ages, tentatively judged to be most reliable, indicate that stratified offshore freshwater plumes originating in distant recharge areas on land were bounded by relatively young saline water that was recharged locally from the overlying estuary. Udenitrified and partially denitrified nitrate of

agricultural or mixed origin was transported laterally beneath the estuary in oxic and suboxic fresh ground water. Ammonium produced by anaerobic degradation of organic matter in estuarine sediments was transported downward in suboxic saline ground water around the freshwater plumes. Many of the chemical and isotopic characteristics of the subestuarine ground waters are consistent with conservative mixing of the fresh (terrestrial) and saline (estuarine) endmember water types. These data indicate that freshwater plumes detected by geophysical surveys beneath Indian River Bay represent lateral continuations of the active surficial nitrate-contaminated freshwater flow systems originating on land, but they do not indicate directly the magnitude of fresh ground-water discharge or nutrient exchange with the estuary. There is evidence that some of the terrestrial ground-water nitrate is reduced before discharging directly beneath the estuary. Local estuarine sediment-derived ammonium in saline pore water may be a substantial benthic source of nitrogen in offshore areas of the estuary.

INTRODUCTION

Submarine or subestuarine discharge of ground water could be a source of nitrogen in coastal waters, but little is known about its distribution or magnitude. Discharging fresh ground water might contain dissolved constituents derived from recharge areas on land, while discharging saline ground water might contain constituents derived from recharge beneath the ocean or estuary. Both types also contain constituents derived from reactions with aquifer materials, but these reactions may vary depending on the salinity and redox status in the recharge area and the hydrogeologic conditions along the ground-water-flow paths. Submarine or subestuarine ground-water discharge commonly is focused in a narrow zone near the shoreline, but offshore springs and other evidence indicate that freshwater also can be found far from shore.

Purpose and Scope

This report presents results of part of a larger study of the distribution and nutrient status of subestuarine ground water in coastal bays of the Delmarva Peninsula (Bratton and others, in press; Krantz and others, in press; Manheim and others, in press). The larger study is aimed broadly at understanding the role of ground-water/surface-water interactions in the health of coastal marine ecosystems. It includes seismic and streaming resistivity surveys of several coastal bays to determine the vertical and spatial distribution of sedimentary features and freshwater bodies beneath the estuaries. The larger study also includes coring and pore-water analyses to determine local vertical distributions of sediment properties along with salinity and concentrations of nitrogen, phosphorus, and silica in the shallow ground water. The current study was designed specifically to investigate the use of environmental tracers and isotopes to determine sources of water and nutrients, transport directions and rates, and biogeochemical reactions affecting nutrient species in subestuarine ground waters. This study was conducted in Indian River Bay, Delaware, in cooperation with the Delaware Department of Natural Resources and Environmental Control.

This report presents a comprehensive set of chemical and isotopic analyses of fresh and saline ground-water samples that were pumped from representative parts of the complex flow system underlying Indian River Bay 75 to 300 m offshore at depths of 3 to 22 m below the sediment-water interface. The chemical and isotopic data are compared with the geophysical results and evaluated with respect to the sources and ages of the ground waters and major dissolved constituents, including nitrogen species. The data, though derived from relatively few samples, can be used to test hypotheses about flow patterns and nutrient transport in offshore ground waters beneath a coastal estuary.

Description of Study Area

The current study was conducted near the southern shore of Indian River Bay in southeastern Delaware (fig. 1). The surficial aquifer in the study area is the Columbia aquifer, which includes the Pliocene Beaverdam Formation and the overlying Pleistocene Omar Formation. These units have lithologies ranging from fluvial-deltaic sand and gravel (generally lower in the section) to marginal marine sand and silty sand (generally higher in the section). The Columbia aquifer is known to be contaminated with NO_3^- (nitrate) in some areas (Hamilton and others, 1993). Concentrations of NO_3^- range from about 30 to 970 $\mu\text{mol/L}$ (average = $460 \pm 370 \mu\text{mol/L}$) at depths of around 10-30 m within the "Holts Neck" subwatershed that discharges to Indian River Bay from the south (Andres, 1992) (A.S. Andres, Delaware Geological Survey, written commun., 2003). The base of the surficial aquifer is defined locally by a compacted silty layer at a depth of around 25-30 m, as indicated by drilling records and gamma logs in the study area (Krantz and others, in press). Along the margins of Indian River Bay within 100 m of shore, Holocene sediments overlying the aquifer commonly consist of less than 1 m of muddy sand. Small incised valleys in the pre-Holocene surface may be 2-3 m deep, and are generally filled with peat overlain by silt and capped with a thin veneer of muddy sand. The Holocene infill sequence thickens substantially offshore to approximately 15 m of silt in the incised valley of Indian River.

Streaming resistivity surveys in the Indian River estuary indicate complex patterns of salinity variation in subestuarine ground water between about 0 and 30 m below the sediment-water interface (Krantz and others, in press; Manheim and others, in press). Apparent interfaces between fresh and saline waters range from horizontal to vertical, and may be relatively abrupt or more gradual. The 3000-m section of resistivity transect DE-R-05 from north of Walter Point to Ellis Point (fig. 2) shows distinct zones of high resistivity that are interpreted as fresh ground-water bodies originating onshore, alternating with zones of low resistivity that are interpreted as saline water. The two most prominent freshwater zones, from 1,000 to 1,450 m and from 2,250 to 2,800 m along the transect, coincide spatially with subestuarine incised valleys that are the offshore extensions of modern tributary streams occupied by tidal marshes. Another small freshwater zone, from 1,800 to 2,000 m, is aligned with a small stream that has been modified for a boat basin. Sections of the White Neck shoreline with low-relief headlands (generally less than 2-m elevation), such as Holts Landing from 2,000 to 2,250 m and a narrow headland between 1,450 and 1,750 m, are characterized by low-resistivity (saline) water in the upper 10 to 15 m of the transect. Saline water may also appear deep within the resistivity transect, for example, below 25 m in the section between 1,800 and 2,200 m.

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with the tritium-helium analyses. Karen Savidge (University of Delaware) provided nutrient analyses. Daniel Phelan, Eurybiades Busenberg, Scott Andres (Delaware Geological Survey), and Richard Greene (Delaware Department of Natural Resources and Environmental Control) provided constructive comments on earlier versions of the manuscript.

METHODS OF INVESTIGATION

Field geophysical studies to determine the distributions of fresh and saline ground waters beneath Indian River Bay are described in detail elsewhere (Krantz and others, in press; Manheim and others, in press). The following sections give a brief overview of the procedures used to select representative ground-water collection sites, obtain the ground-water samples, and analyze them chemically and isotopically.

Drilling, Geophysical Logging, and Well Installation

The coring operation was conducted in October 2001 at four sites offshore from White Neck near Holts Landing designated as WN1, WN2, WN3, and WN4 (fig. 3). The four sites were selected for coring, geophysical logging, and ground-water sampling, on the basis of the streaming resistivity data (figs. 2 and 3). The first two coring sites (WN1 and WN2) represent end-member conditions interpreted from the resistivity profiles; the third and fourth sites (WN3 and WN4) complete an onshore-offshore transect from the margin to the center of Indian River Bay. Site WN1 was approximately 150 m from the shoreline in an area of low subsurface resistivity, which was interpreted to indicate an area with little or no fresh ground-water discharge. Sites WN2 (75 m from the shoreline) and WN3 (300 m from the shoreline) were in an area with high subsurface resistivity, interpreted as an area of potential fresh ground-water discharge, that coincided with a small incised valley identified on seismic profiles. Site WN4, in the middle of Indian River Bay approximately 1000 m offshore from Ellis Point, was in the axis of the main stem of the incised valley of Indian River

identified from seismic data (Krantz and others, in press). The three main components of the coring operation at each site were (1) hydraulic vibracoring to recover sediments; (2) geophysical logging of the corehole; and (3) sampling of the pore fluids from the cores and *in situ* sampling of ground water at the core site. Vibracoring, geophysical logging, and ground-water sampling were completed at sites WN1, WN2, and WN3. Site WN4 was occupied for half a day before demobilizing, and only the borehole geophysical logging was completed at that site.

The order of operations at WN1, WN2, and WN3 was to recover the core, run a gamma log of the hole, temporarily set polyvinyl chloride (PVC) casing in the hole to run an electromagnetic-induction (EM) log, interpret the gamma and EM logs, and choose specific depths for sampling ground water. A hydraulic vibracoring rig developed by MPI Drilling was used for coring, setting casing for geophysical logging, and advancing drivepoints for ground-water sampling. The drill rig is self-contained on a small trailer that was mounted over the edge of an 18-m long construction barge operated by the State of Delaware. The barge can operate in water as shallow as 0.5 m and has spuds to stabilize the vessel on the drilling site. The core barrel was standard NQ steel pipe with 7-cm outer diameter in 1.5-m long flush-threaded sections. Geophysical logs down the coreholes were recorded using a Mount Sopris Instruments MGX II portable digital logger running MSLog software, with a PGA-1000 gamma-logging tool and a PIA-1000 EM probe. The gamma readings were made through the steel core barrel, which was advanced with a solid, conical drive point. The EM conductivity readings were made through 5-cm diameter PVC casing that was closed at the bottom. The PVC casing was set by first drilling HQ steel core barrel (9-cm outer diameter) with a PVC knock-out drivepoint, inserting the PVC casing and filling it with freshwater, and then retracting the outer steel core barrel. The PVC casing filled with freshwater was pulled from the hole after the EM logging was completed. Ground-water samples for geochemical analyses were collected after moving the barge about 2 to 5 m relative to the corehole location, then sequentially advancing the NQ steel core barrel with a 25-cm screened drive point to each of

three depths selected by reviewing the gamma and EM logs. Individual drivepoint samples were named in the field by the corehole site and the mid-screen depth below the bottom of the bay in feet. For example, sample WN1-71 is from site WN1 at a mid-screen depth of 71 ft (feet) below the sediment-water interface.

Water Sampling and Analysis

Subestuarine ground-water samples were collected from discrete depths by pumping from the short-screened drivepoint. The geophysical logs were used to select sampling depths that represented different ground-water masses (varying salinities based on EM logs) and that were relatively likely to yield water at reasonable pump rates (avoiding clay-rich intervals indicated by high gamma activities). The drivepoint wells were developed and purged using a Waterra inertial lift pump with the inlet held above the screen until the water was clear of turbidity and dissolved oxygen measurements were stable. With the exception of Sites WN1-10 and WN3-61, samples were pumped subsequently through two parallel discharge tubes (nylon and copper) from the level of the well screen using a submersible Bennett pneumatic piston pump. The copper discharge line was used mainly for sampling chlorofluorocarbons (CFCs) and other dissolved gases, and the nylon line was used for most of the other chemical and isotopic samples. Sites WN1-10 and WN3-61 were sampled through a single discharge line consisting of nylon and Viton tubing with a peristaltic pump at the surface. Lubricants in the threads of the steel drivepoint casing were removed by steam cleaning after sampling was completed at Site WN1-25. For comparison to the ground-water samples collected in October 2001, representative surface-water samples were collected from Indian River Bay at Holts Landing in October 2001 and September 2002, and from Rehoboth Beach in May 2002.

In October 2001, specific conductance, pH, and O₂ (dissolved oxygen) were measured in the field using WTW pH/conductivity and pH/O₂ meters. One Winkler titration was performed to verify the calibration of the O₂ meter. Specific conductance, pH, O₂, and temperature were measured in a closed flow-through chamber to avoid contact with air.

Chloride concentrations were measured in the field with a Hach field testing kit. Field alkalinities were determined by incremental titrations using a WTW pH meter and Hach titrator. Salinities of surface-water samples collected in 2002 were determined in the laboratory with a YSI specific conductance meter calibrated against IAPSO standard seawater with a salinity of 35.00 g/kg.

Samples for analysis of sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), strontium (Sr), boron (B), iron (Fe), manganese (Mn), silicon (Si, reported as SiO₂), chloride (Cl⁻), bromide (Br⁻), sulfate (SO₄²⁻), nitrate (NO₃⁻), and alkalinity were filtered in the field (0.45 µm) and analyzed in the USGS Water Chemistry Laboratory in Reston, Virginia (Michael Doughten, USGS, written commun., 2002). Cation samples were acidified with Ultrex nitric acid and analyzed by direct-current plasma spectrometry (ARL SpectraSpan V). Anions were analyzed by ion chromatography (Dionex DX-120), and alkalinities were measured with a Radiometer Analytical Titrator system autotitrator. Uncertainties are estimated to be approximately ± 5-10 percent for the reported inorganic constituents (Michael Doughten, USGS, written commun., 2002). Calculated ion charges for the major species generally were balanced to within a few percent.

Samples for dissolved nutrient analyses were filtered in the field (0.2 µm) and frozen before being analyzed at the University of Delaware (Karen Savidge, University of Delaware, written commun., 2001). Dissolved ammonium (NH₄⁺), nitrate plus nitrite (NO₃⁻ + NO₂⁻, abbreviated NO₂₊₃), and phosphate (PO₄³⁻), were analyzed by automated colorimetry using an O/I Analytical Flow Solution IV Analyzer. Concentrations of NH₄⁺ were determined by the phenol hypochlorite method (Grasshoff and Johansen, 1972; Glibert and Loder, 1977). NO₂₊₃ concentration was determined by the sulphanimide/N(1-naphthyl) ethylene diamine method after cadmium reduction of NO₃⁻ to NO₂⁻ (Glibert and Loder, 1977). PO₄³⁻ was determined by the phosphomolybdenum blue method (Strickland and Parsons, 1972). Typical precisions for analyses of NH₄⁺, NO₂₊₃, and PO₄³⁻ were approximately ± 0.2-1, ± 1-5, and ± 0.02-0.05 µmol/L, respectively (Karen Savidge, University of Delaware, written commun., 2002).

Samples to be analyzed for major dissolved gases argon (Ar), nitrogen (N₂), oxygen (O₂), and methane (CH₄) were collected in 125-mL serum bottles, preserved with potassium hydroxide (KOH, 2 pellets, or approximately 200 mg), and sealed with blue butyl rubber stoppers (Bellco) without headspace. Gas analyses were done by gas chromatography (GC) on low-pressure headspace in the USGS Dissolved-Gas Laboratory in Reston, Virginia (Plummer, 2003). Samples to be analyzed for CFCs (CFC11, CFC12, and CFC113) were collected through copper tubing into flame-sealed glass ampules under pure N₂ headspace (Busenberg and Plummer, 1992). CFCs were extracted by a purge-and-trap procedure and analyzed by GC with an electron-capture detector in the USGS CFC Laboratory in Reston (Plummer, 2003). For each sample, the measured concentrations of CFC11, CFC12, and CFC113 were converted to equilibrium partial pressures at sea level after accounting for the measured salinity and for the equilibration temperature and excess air concentration indicated by major dissolved-gas data (Eurybiades Busenberg, USGS, written commun., 2003) (see section in this report on Calculation of Recharge Temperature, Excess Air, and Excess Nitrogen). The equilibrium partial pressures in the samples (given as atmospheric mixing ratios in parts per trillion by volume, pptv) were compared to the atmospheric CFC record to determine the apparent year in which the water last equilibrated with air, referred to as the recharge date (Plummer and Busenberg, 2000). Samples for sulfur hexafluoride (SF₆) analysis were collected unfiltered in 2-L glass bottles with polyseal caps without headspace. In the laboratory, an aliquot for analysis was taken from each of two bottles and the analyses were done by purge-and-trap GC (Busenberg and Plummer, 2000; Plummer, 2003). For each sample, the SF₆ concentration was converted to an equilibrium partial pressure at sea level (atmospheric mixing ratio in pptv) after accounting for the measured salinity and for the equilibration temperature and excess air concentration indicated by the dissolved-gas data (Eurybiades Busenberg, USGS, written commun., 2003).

Samples for helium (He), neon (Ne), and tritium-helium age determination were collected in flow-through copper tubes that

were crimp-sealed in the field. He and Ne were extracted for mass-spectrometric analysis, then degassed aliquots of the water were re-analyzed after several months to determine tritium (^3H) concentrations from helium-3 (^3He) in-growth at the Lamont-Doherty Earth Observatory Noble Gas Laboratory (LDEO), Palisades, New York (Ludin and others, 1998). Additional samples for ^3H analysis were collected unfiltered in bottles with polyseal caps. Some of these samples (mainly ground-water replicates for the copper tubes) were analyzed by ^3He in-growth at LDEO, and others (mainly surface waters) were analyzed by liquid scintillation counting after electrolytic enrichment at the USGS Tritium Laboratory in Menlo Park, California with uncertainties of approximately ± 0.3 - 0.5 TU (R.L. Michel, USGS, written commun., 2002).

The age of each ground-water sample (in years since the time it left contact with air) was assumed to be equal to the time indicated by radioactive decay of ^3H to ^3He in a closed system, after adjusting the measured ^3He concentration for atmospheric gas contributions and for excess terrigenic He (Schlosser and others, 1998) with an assumed $^3\text{He}/^4\text{He}$ ratio of 2×10^{-8} (Mamyrin and Tolstikhin, 1984). Temperatures used to calculate atmospheric contributions were determined from the concentrations of Ar and Ne, assuming those gases had only atmospheric sources (see section on Calculation of Recharge Temperature, Excess Air, and Excess Nitrogen). For each sample, the concentrations of ^3H and tritiogenic ^3He ($^3\text{He}[\text{trit}]$) were converted to ratios of $^3\text{H}/^3\text{H}^0$, where $^3\text{H}^0$ is the initial ^3H concentration ($^3\text{H}^0 = ^3\text{H} + ^3\text{He}[\text{trit}]$), and used to calculate the closed-system ^3H - ^3He radioactive decay age (t):

$$t = -1/\lambda \cdot \ln(^3\text{H}/^3\text{H}^0), \quad [1]$$

where λ is the ^3H decay constant (0.055764/year).

Stable isotopic compositions of H, O, and N were analyzed as $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{15}\text{N}$ values, respectively (generalized as $\delta^i\text{E}$, expressed in per mil or ‰):

$$\delta^i\text{E} = (R_x/R_{\text{ref}} - 1) \cdot 1000 \text{ ‰}, \quad [2]$$

where R refers to the isotopic mole ratio of $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$, or $^{15}\text{N}/^{14}\text{N}$, x refers to the

sample, and ref is the primary reference material for which the δ value is defined as 0. The primary reference materials are VSMOW (Vienna Standard Mean Ocean Water) for H and O, and “air” (atmospheric N_2) for N. Samples to be analyzed for H and O isotopes of water were collected in 60-mL glass bottles and analyzed at the USGS Reston Stable Isotope Laboratory in Reston, Virginia (Coplen, 2003) by H_2 and CO_2 equilibration and mass spectrometry. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were normalized to the VSMOW-SLAP scale (Coplen, 1988) with uncertainties of about ± 1 ‰ and ± 0.1 ‰ (1σ), respectively. For N isotope analyses of NH_4^+ , filtered water samples were treated with magnesium oxide (MgO) and the resulting ammonia (NH_3) was distilled from the water and collected in a dilute acid solution that was dried and then oxidized chemically to produce N_2 . The N_2 was analyzed by mass spectrometry for the USGS National Water Quality Laboratory by the ZymaX Isotope Laboratory, San Luis Obispo, California. For N isotope analyses of NO_3^- , filtered freshwater samples were freeze-dried and the salts were baked in evacuated sealed glass tubes with $\text{Cu}+\text{Cu}_2\text{O}+\text{CaO}$, then the N_2 gas produced in the tubes was expanded into a dual-inlet isotope-ratio mass spectrometer in the USGS Reston Stable Isotope Laboratory (Böhlke and Denver, 1995). Sediment samples were dried, ground, and homogenized, then baked and analyzed like the NO_3^- samples. N isotope data for NH_4^+ , NO_3^- , and sediment were normalized to $\delta^{15}\text{N}$ values of $+0.4$ ‰ for IAEA-N1 and $+180$ ‰ for USGS-32 (Böhlke and Coplen, 1995). For N isotope analyses of dissolved ground-water N_2 , the headspace gas remaining in each 125-mL serum bottle after GC analysis was sealed into a pair of evacuated glass tubes with reagents, baked, and analyzed against samples of N_2 in air ($\delta^{15}\text{N} = 0.0$ ‰) and laboratory-equilibrated water ($\delta^{15}\text{N} = +0.7 \pm 0.1$ ‰). The overall uncertainties of the normalized N isotope analyses are estimated to be approximately ± 0.2 - 0.3 ‰ for NH_4^+ and NO_3^- , and ± 0.1 ‰ for N_2 .

Calculation of Recharge Temperature, Excess Air, and Excess Nitrogen

The apparent recharge temperature and amount of excess air were calculated for each

sample from the concentrations of Ar and Ne by assuming two atmospheric dissolved-gas components (Aeschbach-Hertig and others, 1999; Stute and Schlosser, 2000): (1) from air equilibration at the elevation of the water table and 100-percent relative humidity; and (2) from unfractionated excess air introduced during recharge or sampling. This calculation was completed for each sample by solving iteratively an equation relating the measured concentrations of Ar and Ne to a common equilibration temperature and concentration of $\text{air}_{\text{excess}}$ (excess air):

$$\begin{aligned} \text{air}_{\text{excess}} \text{ in ccSTP/L} &= \{[\text{Ar}]_{\text{meas}} - [\text{Ar}(\text{T},\text{S},\text{elev})]_{\text{asw}}\} / \\ &\quad 0.417 \mu\text{mol}_{\text{Ar}}/\text{ccSTP}_{\text{air}} \\ &= \{[\text{Ne}]_{\text{meas}} - [\text{Ne}(\text{T},\text{S},\text{elev})]_{\text{asw}}\} / \\ &\quad 0.000811 \mu\text{mol}_{\text{Ne}}/\text{ccSTP}_{\text{air}}, \end{aligned} \quad [3]$$

where $[\text{Ar},\text{Ne}]_{\text{meas}}$ is the measured concentration of Ar or Ne in the sample (in $\mu\text{mol/L}$) and $[\text{Ar},\text{Ne}(\text{T},\text{S},\text{elev})]_{\text{asw}}$ is the concentration of Ar or Ne in air-saturated water at the appropriate temperature, salinity, and elevation (sea level for these samples), calculated using Ar and Ne solubility data (Weiss, 1970, 1971). The quantity ccSTP refers to cubic centimeters of gas at standard temperature (0°C , or degrees Celsius) and pressure (1 atmosphere).

Concentrations of N_2 that are in excess of the amounts attributable to atmospheric sources may be the result of denitrification. The concentration of $\text{N}_{2,\text{excess}}$ (excess N_2 attributable to denitrification) was calculated for each sample by using the recharge temperature and $\text{air}_{\text{excess}}$ value derived from Ar and Ne data:

$$\begin{aligned} \text{N}_{2,\text{excess}} \text{ in } \mu\text{mol/L} &= [\text{N}_2]_{\text{meas}} - [\text{N}_2(\text{T},\text{S},\text{elev.})]_{\text{asw}} - \\ &\quad [\text{air}_{\text{excess}} \text{ in ccSTP/L}] \cdot 34.8 \mu\text{mol}_{\text{N}_2}/\text{cc}_{\text{air}}. \end{aligned} \quad [4]$$

The detection limit for $\text{N}_{2,\text{excess}}$ based on these calculations and data from this study is estimated to be approximately $10 \mu\text{mol/L}$ (equivalent to $20 \mu\text{mol/L}$ denitrified NO_3^-). For some samples lacking reliable Ne data, estimates of recharge temperatures, $\text{air}_{\text{excess}}$, and $\text{N}_{2,\text{excess}}$ were based on Ar and N_2 concentrations and inter-sample comparisons, resulting in larger detection limits of around $20\text{-}30 \mu\text{mol/L}$ for $\text{N}_{2,\text{excess}}$.

ISOTOPE GEOCHEMISTRY AND CHRONOLOGY OF GROUND-WATER SAMPLES

Results of analyses and calculations are summarized in table 1 and table 2 for water samples and sediment samples, respectively. For some of the analytes in table 1, such as the major dissolved gases, CFCs, and SF_6 , individual results are given for field replicates collected in multiple containers. For some analytes and calculated values such as salinity, ^3H , and recharge temperature, results are given for more than one analytical method. In both of these situations, “selected” values are also given. The “selected” values represent either averages or choices based on critical evaluation of the data. An overview of the ground-water dating results is given in table 3.

Major-Element Chemistry and Water Isotopes

Patterns of salinity variation in subestuarine ground water were inferred from electromagnetic logging in the vertical boreholes (fig. 3). The measured salinities in the pumped ground waters confirmed the geophysical results indicating that saline ground water similar to Indian River Bay surface water was present throughout most of the sampled interval at site WN1, whereas large intervals of freshwater were present at intermediate depths at sites WN2 and WN3 (fig. 3; table 1). Freshwater with Cl^- concentrations less than 20 mmol/L (millimole per liter) was sampled 75 and 300 m offshore beneath the bay at depths of around 10-16 m below the sediment-water interface at sites WN2-35, WN2-53, and WN3-34. None of the ground-water samples had salinity higher than Indian River Bay surface water, which was between 80 and 90 percent of standard seawater salinity (35 g/kg) in samples collected during October 2001 and September 2002. Thus, there is no evidence in these samples for intrusion or discharge of undiluted seawater or brine.

Ratios of major inorganic species (Na/Cl^- , K/Cl^- , Mg/Cl^- , Ca/Cl^- , Sr/Cl^- , B/Cl^- , Br/Cl^- , and $\text{SO}_4^{2-}/\text{Cl}^-$) in the ground waters generally were consistent with two-component mixtures of freshwater and estuarine surface

water (fig. 4). Even alkalinity is roughly correlated with salinity, and that trend is consistent with generally small amounts of sulfate reduction and methanogenesis, though both processes appear to have occurred to a limited degree in the saline ground waters. SiO₂ concentrations are inversely correlated with salinity, consistent with mixing of water sources and minor additions attributable to water-rock interactions (fig. 4).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of fresh ground waters are consistent with a local meteoric water line defined by $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 14$ (fig. 5A). Andres (1991) reported 27 analyses of fresh ground waters from onshore wells in the Rehoboth Bay and Indian River Bay watersheds with average values of -38.0 ± 3.6 ‰ for $\delta^2\text{H}$ and -6.27 ± 0.58 ‰ for $\delta^{18}\text{O}$, which are similar to the freshwater endmember values in the Indian River Bay subestuarine ground-water dataset (fig. 5A). These data are consistent with results from other shallow aquifers in the Mid-Atlantic Coastal Plain, including some from an agricultural site near Fairmount, Delaware (fig. 5) (Dunkle and others, 1993). Correlations among $\delta^2\text{H}$, $\delta^{18}\text{O}$, and Cl⁻ for all of the subestuarine ground waters are consistent with mixing between fresh meteoric water and saline estuarine surface water (fig. 5). Furthermore, the estuarine surface-water samples plot on a mixing line between fresh meteoric water and standard open-ocean seawater ($\delta^2\text{H} = 0.0$, $\delta^{18}\text{O} = 0.0$, Cl⁻ = 560 mmol/L). These data are interpreted to mean that the saline ground water was recharged locally beneath the estuary, and the surface water in the bay was a brackish mixture of seawater and fresh meteoric-water discharge from streams and ground water. The isotope data do not indicate substantial amounts of evaporation of the estuarine surface water before it entered the subsurface. A single sample collected May 12, 2002 from the ocean at Rehoboth Beach was on the same mixing line with $\delta^2\text{H}$, $\delta^{18}\text{O}$, and Cl⁻ values slightly higher than those of the estuary.

Dissolved Gases, Nitrogen Species, and Nitrogen Isotopes

Concentrations of Ne, Ar, and N₂ were used to estimate recharge temperatures, amounts of air_{excess} attributable to incorporation of air during recharge or sampling, and amounts of N_{2,excess} attributable to

denitrification. In samples from sites WN1-71, WN2-53, and WN2-68, all three gases yielded internally consistent temperatures and air_{excess} concentrations, with no evidence of denitrification. Samples from site WN2-35 indicated a significant amount of N_{2,excess} with values of temperature and air_{excess} that were similar to the values at other sites. In contrast, samples from site WN3-34 (and possibly WN3-61) yielded discordant results with anomalous temperatures indicating that the He-Ne samples from those sites may have been partially degassed, possibly during sample collection.

Overall, the dissolved gas data generally indicate that the fresh ground waters were recharged at approximately 10-11 °C with air_{excess} concentrations of 0-2 ccSTP/L, whereas saline ground waters were recharged at approximately 14-16 °C with 0-1 ccSTP/L of air_{excess} (table 1; fig. 6). By comparison, the mean annual air temperature at Georgetown, Delaware (12 miles northwest of Indian River Bay) from 1976-1995 was approximately 12.9 °C (mean monthly averages ranged from 0.8-24.7 °C) (UDCANR, 2003); the mean annual soil temperature at 2 m depth at Cape Henlopen, Delaware from 1997-2001 was approximately 14 °C (monthly values ranged from about 11-17 °C) (Wehmiller and others, 2000); and the mean annual water temperature in Indian River Bay from 1989-1992 was about 17.5 °C (ranging from about 5-30 °C) (William Ullman, University of Delaware, written commun., 2002). The average difference between the inferred recharge temperatures of fresh and saline ground-water samples is qualitatively consistent with the slightly higher average temperature of Indian River Bay water compared to air and soil temperatures on land, but the recharge temperatures in both ground-water types apparently are biased slightly to lower values. The small difference in the average air_{excess} concentrations may be attributed to differences in the recharge processes of the fresh and saline ground waters. Fresh ground water recharging beneath an unsaturated zone on land may be expected to incorporate more air from dissolution of trapped bubbles than saline ground water recharging beneath the standing water and saturated sediments in the estuary.

Samples from only two sites had substantial concentrations of O₂ and NO₃⁻ (table 1; fig. 7): WN2-53 and WN3-34 had 26

to 115 $\mu\text{mol/L}$ O_2 (GC analyses) and 51 to 108 $\mu\text{mol/L}$ NO_3^- with $\delta^{15}\text{N}[\text{NO}_3^-]$ values of 5.3 to 6.4 ‰. Both of these samples were freshwater and neither appears to have had $\text{N}_{2,\text{excess}}$; thus, these samples provide evidence for transport of NO_3^- from onshore recharge areas to subestuarine positions in the aquifer without substantial NO_3^- reduction. The $\delta^{15}\text{N}$ values are within the range commonly observed in NO_3^- beneath fertilized agricultural fields in the Mid-Atlantic region, but they are lower than most values observed in areas dominated by manure or septic system sources of NO_3^- (Böhlke and Denver, 1995; Kendall and Aravena, 2000; Böhlke, 2002, in press).

The freshwater sample from site WN2-35 had no measurable O_2 or NO_3^- , but contained an estimated 29 $\mu\text{mol/L}$ of $\text{N}_{2,\text{excess}}$ (equivalent to 58 $\mu\text{mol/L}$ of denitrified NO_3^-). This sample also had an anomalously high value of $\delta^{15}\text{N}[\text{N}_2]$ (+1.1 ‰) compared to the other samples, which had $\delta^{15}\text{N}[\text{N}_2] = +0.6$ to $+0.9$ ‰ (approximately consistent with air equilibration). The gas isotopes confirm that the sample from site WN2-35 had a substantial component of non-atmospheric N_2 , which is interpreted as a product of denitrification. This sample provides evidence that some of the NO_3^- transported beneath the estuary was reduced within the aquifer before mixing with saline ground water or discharging. The $\delta^{15}\text{N}$ value of the non-atmospheric $\text{N}_{2,\text{excess}}$ component is poorly defined because of the much larger component of atmospheric N_2 in the sample, but it could be consistent with the $\delta^{15}\text{N}$ values of the NO_3^- in the oxic samples, indicating a similar source of NO_3^- in the corresponding recharge. In the WN2 profile, denitrified ground water occurred above undenitrified ground water within the freshwater wedge; however, the location of active denitrification and the identity of the electron donor(s) are not known. There is no evidence for $\text{N}_{2,\text{excess}}$ attributable to denitrification in the saline ground waters, given a detection limit of around 10 to 20 $\mu\text{mol/L}$ (20 to 40 $\mu\text{mol/L}$ of NO_3^- equivalent).

Concentrations of NH_4^+ were 49 to 76 $\mu\text{mol/L}$ in the pumped saline ground waters, but less than 3 $\mu\text{mol/L}$ in the fresh ground waters. Similarly, concentrations of CH_4 were 0.3 to 0.7 $\mu\text{mol/L}$ in the saline ground waters, but less than 0.1 $\mu\text{mol/L}$ in the fresh ground waters. These differences may be attributed to the contrasting origins of the fresh and saline

pumped ground waters: (1) the fresh ground waters were recharged on land with O_2 and NO_3^- and subsequently were reduced partially in the aquifer, but not to the point of NH_4^+ or CH_4 production; and (2) the saline ground waters were recharged beneath the estuary and acquired NH_4^+ and CH_4 while passing through reduced organic-rich sediments beneath the estuary. Pore waters squeezed from shallow sediment cores at sites WN2 and WN3 have a wide range of NH_4^+ concentrations from about 160 to 930 $\mu\text{mol/L}$ (fig. 7; Bratton et al., in press). The highest concentrations are in the saline pore waters overlying the freshwater plume, but some of the freshwaters near the upper boundary of the plume also appear to have substantial amounts of NH_4^+ . These data may indicate a source of NH_4^+ in the fresh ground water near the top of the plume, possibly from recharge in marginal wetlands or reactions in shallow nearshore aquifer materials.

Three of the deep saline ground-water samples had $\delta^{15}\text{N}[\text{NH}_4^+]$ values of +2.8 to +4.5 ‰ (table 1). Shallow Holocene sediment samples had N concentrations ranging from about 60 to 12,000 mg/kg with $\delta^{15}\text{N}[\text{N-total}]$ values of -1 to +5 ‰, while deeper Pleistocene sediments had N concentrations generally less than about 20 mg/kg with unmeasurable $\delta^{15}\text{N}$ (table 2). The overall similarity of the $\delta^{15}\text{N}$ values of aqueous NH_4^+ and Holocene sediment N indicates that the NH_4^+ in the saline ground water may have been produced by mineralization of organic matter in shallow sediments undergoing diagenesis. It is commonly observed or assumed that NH_4^+ released from organic matter by microbial degradation has a $\delta^{15}\text{N}$ value about equal to or slightly lower than the $\delta^{15}\text{N}$ value of the organic N source, which may increase as a result (Fogel and Cifuentes, 1993; Macko and others, 1993; Nadelhoffer and Fry, 1994). However, Lehman and others (2002) show that the $\delta^{15}\text{N}$ values of bulk organic pools can also decrease during anoxic degradation and bacterial growth. A semi-logarithmic inverse correlation between N concentration and $\delta^{15}\text{N}$ in the Holocene sediments from Indian River Bay could be consistent with varying degrees of N loss by a process yielding a product such as NH_4^+ that is slightly depleted in ^{15}N (fig. 8). If it were assumed that the variations in the N concentrations and $\delta^{15}\text{N}$ values of the

sediments were caused by progressive N loss, then an apparent isotope fractionation factor for the loss process could be derived by fitting the array of sediment data to an approximation of the Rayleigh fractionation equation:

$$\delta^{15}\text{N} \approx \delta^{15}\text{N}^{\circ} + \varepsilon \cdot \ln(C/C^{\circ}), \quad [5]$$

where C° and $\delta^{15}\text{N}^{\circ}$ are the average N concentration and $\delta^{15}\text{N}$ value of the least-reacted samples with the most N (fig. 8). The apparent isotope fractionation factor (ε) derived from the sediment data is -1.8‰ . The $\delta^{15}\text{N}[\text{NH}_4^+]$ values of 3 of the deeper ground-water samples are about 4-5 ‰ higher than the $\delta^{15}\text{N}$ values of the most N-rich sediments, but similar to those of sediments with low-to-intermediate N concentrations (fig. 8). These data could indicate that (1) the deeper ground-water NH_4^+ was derived from the shallower organic-rich sediments and was partly oxidized during or after the mineralization process, resulting in slight ^{15}N enrichment of the NH_4^+ before it moved downward (Hübner, 1986); (2) the deeper ground-water NH_4^+ was produced mainly in sediments with intermediate or relatively low N concentrations; (3) the few analyzed sediment samples are not fully representative; or (4) the apparent fractionation factor derived from the sediment analyses is misleading. A single saline ground-water sample from site WN2-68 yielded a relatively high value of $\delta^{15}\text{N}[\text{NH}_4^+]$ ($+13\text{‰}$). If this value is not an artifact, then it could indicate a different source of NH_4^+ or a relatively large amount of isotopic fractionation by partial oxidation of the NH_4^+ .

Ground-Water Dating by Tritium (^3H)

Of the ground-water dating methods applied in this study, the one based on ^3H concentrations is considered to be the least vulnerable to contamination, degradation, and degassing problems, but it may have relatively large age uncertainties because of the complex history of ^3H in the atmosphere and the relatively poorly known ^3H concentrations in coastal waters in comparison to the long-term record for Washington, D.C. (fig. 9). Concentrations of ^3H in the ground waters pumped from beneath Indian River Bay ranged from 0.3 to 9.3 TU (tritium unit, or 10^{18} ·

$^3\text{H}/^1\text{H}$); however, six of the eight samples had a relatively narrow range of ^3H concentrations between 3.2 and 5.6 TU (average = 4.5 ± 0.9 TU). Though there are no long-term records of ^3H concentrations in waters near the Delaware coast, there is evidence that 4-5 TU may be approximately equal to the average value of “modern” precipitation and recent ground-water recharge in the study area (figs. 9A-B).

Since large-scale thermonuclear bomb testing began in 1952, ^3H concentrations at Cape Hatteras, North Carolina have been substantially lower than in Washington, D.C., partly because of the greater influence of low- ^3H marine moisture near the coast. In 2000 and 2001, the average concentration of ^3H in precipitation at Cape Hatteras was approximately 5.0 TU, roughly half the average concentration in Washington, D.C. (R.L. Michel, USGS, written commun., 2002). Data reported by Lindsey and others (in press) indicate that four shallow ground-water samples from the headwaters of the Pocomoke River basin with apparent ^3H - ^3He recharge dates in the late 1990s had initial ^3H concentrations ranging from 3.9 to 6.3 TU (averaging 5.4 ± 0.9 TU) (fig. 9B). These data indicate that precipitation contributing to ground-water recharge near the southern border of Delaware had ^3H concentrations about half the average value in precipitation at Washington, D.C. during the same period (approximately 11.5 TU from 1996 to 1999) (IAEA, 1999) (R.L. Michel, USGS, written commun., 2002). Ekwurzel and others (1994) reported ^3H concentrations and ^3H - ^3He ages of ground-water samples indicating that recharge in the Fairmount watershed (west of Rehoboth Bay) had ^3H concentrations ranging from 0.5 to 1.0 times the values recorded in Washington, D.C. in the 1970s and 1980s (fig. 9B). It is possible that the ^3H concentrations in Fairmount ground waters were slightly higher than contemporary values at the coast because of less marine moisture or because the recharge at Fairmount included older irrigation water with bomb ^3H . Assuming the local ^3H concentrations in precipitation and atmospheric moisture near the east coast of Delaware were correlated with those in Washington, D.C., but lower by a factor of about 2 because of proximity to the ocean, it can be shown that ground waters recharged from local precipitation at any time since about the mid-

1970s would have had an average of around 5 TU if sampled in 2001 (fig. 9A). In addition, four samples of saline surface water (29.1 to 31.5 g/kg) collected from the Indian River Bay and Rehoboth Beach in 2001 and 2002 had ^3H concentrations ranging from 3.5 to 7.6 TU (average = 4.9 ± 1.8 TU) (table 1), similar to the inferred values for modern precipitation. Therefore, the available data indicate that estuarine and shallow coastal marine waters may have had ^3H concentrations that were similar to those of local atmospheric moisture and precipitation. Thus, for most of the subestuarine pumped ground-water samples, including both fresh and saline endmembers, ^3H concentrations between about 3 and 6 TU could be interpreted to indicate apparent ages between about 0 and 30 years (post-bomb-peak), 45-50 years (pre-bomb-peak), or possibly mixtures including bomb-peak and pre-bomb waters (fig. 9A).

The highest ^3H concentration (9.3 TU) was obtained for the freshwater sample from site WN2-35. This value is consistent with recharge beneath the land surface by precipitation that fell during the early 1970s, slightly earlier than some of the other samples with 3-6 TU (fig. 9). The lowest ^3H concentration (0.3 TU in the brackish-water sample from site WN3-61) was substantially lower than modern values in precipitation or surface water in the Mid-Atlantic region. This low ^3H concentration indicates that the mixed (brackish) ground water near the lower boundary of the freshwater plume at this offshore site was mainly recharged before 1952, when large-scale atmospheric thermonuclear bomb testing began; that is, the bulk of the water in this sample was more than 50 years old (fig. 9).

Ground-Water Dating by Tritium-Helium (^3H - ^3He)

In comparison to the other environmental gas tracer methods used for ground-water dating, the ^3H - ^3He method is not affected by chemical contamination and degradation, but it is relatively susceptible to errors caused by degassing in pumps and discharge tubing. The ^3H - ^3He data indicate apparent radioactive decay ages ranging from about 2 to 37 years (corresponding recharge

dates from 1965 to 1999). The sample from site WN3-61 had a substantial amount of terrigenic He (29 percent of the total He in the sample) and yielded an adjusted apparent age of 56 years, but should be considered undatable by this method because of its low (pre-bomb) ^3H concentration. No adjustments were made for terrigenic He in the other samples, for which the average of the apparent calculated concentrations of terrigenic He was -0.6 ± 1.9 percent of the total He. Analyses of replicate samples from site WN1-71 were essentially identical, indicating that site yielded water only 2 ± 1 years old. Ages derived from replicate samples from site WN3-34 were in reasonably good agreement (19 years compared to 25 years), despite the fact that the samples apparently were degassed by different amounts (both were substantially undersaturated with respect to Ne). The apparent age of the second replicate (25 years) is considered more reliable because the second replicate was not degassed as much as the first. For most of the samples, the apparent ^3H - ^3He ages are concordant with both the measured ^3H concentrations and the reconstructed initial ^3H concentrations ($^3\text{H}^0$), allowing for minor dispersion of the 1960s bomb peak (fig. 10). For example, the sample from site WN2-35 almost certainly contained recharge from the 1960s with high $^3\text{H}^0$, and the sample from site WN3-61 contained mainly pre-bomb water. The sample from site WN2-53 also apparently contained recharge from the 1960s, but that sample appears to be slightly older than the one from site WN2-35.

Ground-Water Dating by Chlorofluorocarbons (CFCs)

Concentrations of CFC12 indicate ground-water apparent ages of about 26 to 53 years (recharge dates from 1949 to 1976), except at site WN2-53, where the sample apparently was contaminated with CFC12. CFC11 and CFC113 generally indicate relatively old recharge dates and were not detected in some samples that had substantial concentrations of CFC12. These results are consistent with partial degradation of CFCs, beginning with CFC11 and CFC113, as is commonly observed in chemically reduced environments elsewhere (Oster and others, 1996; Plummer and Busenberg, 2000). Oster

and others (1996) presented evidence that the degradation rate of CFC11 is an order of magnitude higher than that of CFC12 in some reduced ground waters. Despite evidence for selective CFC11 and CFC113 degradation beneath Indian River Bay, the CFC12 apparent recharge dates of freshwaters from sites WN2-35 and WN3-34 are roughly consistent with the corresponding ^3H - ^3He ages and ^3H concentrations (fig. 10), and the CFC12 apparent recharge date of saline water from site WN3-61 (late 1940s) is qualitatively consistent with the low (pre-bomb) concentration of ^3H in that sample. Furthermore, in each of the three profiles, CFC12 apparent ages increase downward, and the CFC12 apparent ages of the deep saline samples increase slightly with distance offshore, as do the CFC12 apparent ages of the freshwater samples. On the basis of these data and comparisons, it is concluded that CFC11 and CFC113 were partially to completely degraded and should not be used in the evaluation of the ground-water ages. The CFC12 data may be useful, but the CFC12 may also be partially degraded.

Ground-Water Dating by Sulfur Hexafluoride (SF_6)

Concentrations of SF_6 indicate ground-water apparent ages of about 2 to 24 years (recharge dates from 1977 to 2000), except for site WN1-25, which was contaminated with SF_6 . The SF_6 ages were slightly to moderately younger than the CFC12 and ^3H - ^3He ages in two fresh ground-water samples, and much younger in three saline ground waters. Mixing ground waters of varying ages could account for the relatively small discrepancies in the freshwater samples, but cannot account for the larger discrepancies in the saline samples (fig. 10). Other possible reasons for SF_6 ages being younger than CFC12 ages include CFC12 degradation and excess SF_6 . Observations that could be interpreted as evidence for CFC12 degradation include (1) the apparent age discrepancies are larger in saline samples, which are anoxic and have relatively high concentrations of NH_4^+ and CH_4 , conditions that may be associated with degradation of CFC12 (Oster and others, 1996; Rowe and others, 1999); and (2) the other analyzed CFCs (CFC11 and CFC113) generally appear to have been

degraded substantially relative to CFC12. Observations that could be interpreted as evidence of excess SF_6 include (1) CFC12 has been shown to be relatively stable in many other aquifers under reducing conditions, even when CFC11 and CFC113 have been degraded (Plummer and Busenberg, 2000); (2) at least one of the samples had a SF_6 concentration substantially higher than that of modern water equilibrated with uncontaminated air; (3) low levels of natural or anthropogenic background SF_6 have been observed in ground water from a variety of hydrogeologic settings including the Mid-Atlantic Coastal Plain (Busenberg and Plummer, 2000); and (4) regionally elevated atmospheric SF_6 concentrations have been documented in some areas (Busenberg and Plummer, 2000). Four samples had relatively uniform SF_6 concentrations averaging 0.33 ± 0.06 fmol/L (femtomoles per liter), indicating apparent recharge dates in the late 1970s. One of those samples (from site WN3-61, with $\text{SF}_6 = 0.23$ fmol/L and $^3\text{H} = 0.3$ TU) must have been recharged mainly before thermonuclear bomb testing in the early 1950s. It would be possible to account for the low concentrations of ^3H and SF_6 in that sample by assuming it was a mixture with about 10 percent young water (less than 5 years old, containing modern concentrations of ^3H and SF_6) and about 90 percent old water (more than 40-50 years old, containing no ^3H or SF_6); however, the ratio of $^3\text{H}/^3\text{H}^0$ would not be consistent with such a mixture. Therefore, the data seem to indicate that there was a consistent low background or contaminant level of SF_6 in the samples and that SF_6 apparent ages of around 22-24 years should be regarded as minimum ages.

Summary of Ground-Water Ages

Ground-water samples generally consist of mixtures of waters with a range of recharge dates. In this study, sampling from drive-point wells with short screens was intended to minimize artificial mixing of ages in the samples, but natural dispersion in the aquifer is likely to have mixed the dating tracers to some degree. Nevertheless, although it is not possible to give a definitive summary of the age distribution of the pumped ground waters because of potential mixing and observed discordance among the various ground-water

dating techniques, it can be concluded that all of the samples (fresh and saline) except the one from site WN3-61 were dominated by water that recharged within the last 50 years (table 3). The most reliable results were obtained from the freshwaters, where apparent age discordance is minimal. For example, site WN2-35 yielded apparent ages of about 30 to 40 years from ^3H , 28 years from CFC12, 23 years from SF_6 , and 34 years from ^3H - ^3He . Data from all three freshwater samples indicate ages at depth that are at least qualitatively consistent with those of freshwater surficial aquifers beneath the Delmarva Peninsula (Dunkle and others, 1993). The two freshwater samples from site WN2 appear to have been stratified, with the deeper sample slightly older than the shallower sample. Brackish water from site WN3-61 (approximately two-thirds fresh and one-third saline) was dominated by water more than 50 years old, which is substantially older than the water from site WN3-34, consistent with age stratification in the freshwater plume at site WN3. Therefore, the age data are consistent with the hypothesis that freshwater underlying Indian River Bay was essentially a continuation of the surficial aquifer that was recharged onshore. More detailed sampling, especially at shallower depths, would be required to define the age gradients and discharge patterns in the subestuarine freshwater.

For some of the saline ground waters, which had relatively high concentrations of CH_4 and NH_4^+ , substantial discordance among the dating techniques is not completely understood. The most important discrepancies are in the deep saline samples from sites WN1-71 and WN2-68. If the ^3H - ^3He data and interpretations for these samples are accurate, then it would appear that CFC12 was degraded by about 64 to 73 percent and SF_6 had a low level of contamination or natural background equivalent to an atmospheric partial pressure of about 0.6 pptv. Anthropogenic contamination could have resulted from drilling and sampling, or it could have been present in Indian River Bay when the saline ground waters were recharged. If the CFC12 results are assumed to be reliable, as they are in many other ground-water systems, then the SF_6 would appear to be contaminated and the concentration of ^3He [trit] would be too low by a factor of about 4 to 20. However, there is no obvious reason to suspect such a bias in the He isotope data.

Apparent deficits of CFC12 in comparison to ^3H - ^3He recharge dates can occur as a result of mixing young water (containing CFC12, ^3H , and ^3He [trit]) with old (pre-tracer) water. The Cl^- and $\delta^{18}\text{O}$ data indicate mixing of saline and fresh ground-water components in some samples, but some of the largest apparent age discrepancies are in samples that are relatively close to the saline endmember (sites WN1-71 and WN2-68). Discordance between the CFC12 and ^3H - ^3He data in these samples could be attributed to mixing of young and old (pre-tracer) saline waters, but this would require that the initial ^3H concentrations of the young fractions were substantially higher than those estimated for the coastal region, and perhaps even slightly higher than the measured values in precipitation in Washington, D.C. (table 1; fig. 10). Although this cannot be ruled out entirely, it would be difficult to reconcile with the other ^3H data from surface waters and young ground waters in the region. Because the saline ground waters also contained substantial amounts of CH_4 and NH_4^+ , and because CFC11 and CFC113 were essentially gone, it is considered likely that CFC12 was at least partially degraded, as observed elsewhere in some anoxic ground-water environments (Oster and others, 1996; Rowe and others, 1999). Therefore, the preferred interpretation of the ground-water ages in this study is based mainly on the ^3H and ^3H - ^3He results (table 3), but the overall uncertainties of these ages or age mixtures are difficult to quantify.

IMPLICATIONS FOR GROUND-WATER MOVEMENT AND NITROGEN TRANSPORT

The results of this study have important implications with respect to fresh and saline ground-water movement and nutrient transport beneath Indian River Bay. In addition, despite the limited number of samples, and some uncertainty in the interpretations of the data, the results provide useful guidance for future studies of offshore freshwater/salt-water interactions in coastal estuaries like Indian River Bay.

Sources and Fate of Dissolved Inorganic Nitrogen in Ground Water

Though limited in number, the data from the pumped subestuarine ground waters indicate that the major dissolved inorganic N species (NO_3^- and NH_4^+) were produced independently under contrasting physical conditions (fig. 11). NO_3^- occurs only in the freshwater plumes and almost certainly was derived from nitrification in unsaturated soils on land. The observed or inferred initial NO_3^- concentrations (51 to 108 $\mu\text{mol/L}$) were substantially higher than what are normally considered to be natural in the region (less than 30 $\mu\text{mol/L}$), but not as high as concentrations observed in young ground waters recharged directly beneath fertilized agricultural fields or septic systems in the region (commonly several hundred to more than one thousand $\mu\text{mol/L}$) (Hamilton and others, 1993; Böhlke and Denver, 1995). The ground-water ages, and the concentrations and isotopic compositions of the NO_3^- , could be consistent with old agricultural ground waters or with mixed land uses in the recharge areas. Parts of the plumes containing younger ground water might have higher concentrations of $[\text{NO}_3^-]^\circ$.

The only evidence for denitrification was in freshwater at site WN2, where the redox gradient in the freshwater plume was inverted (where anoxic, denitrified water was above oxic, NO_3^- -bearing water). It is not known where denitrification occurred, but it must have been downgradient from the recharge area on land, and it apparently was not a result of mixing with reduced saline water. The inverted redox gradient in the freshwater plume at site WN2 might be a local phenomenon related to upgradient wetland or channel-filling sediments, or it may be a more widespread phenomenon related to the overall lithostratigraphic sequence of the pre-Holocene aquifer section.

In contrast, NH_4^+ in the pumped ground water samples was consistently associated with elevated salinity and was most likely derived from diagenesis of sedimentary organic matter under suboxic to anoxic conditions beneath the estuary. Surficial Holocene sediments have the highest concentrations of organic N and pore-water NH_4^+ , whereas the underlying pre-Holocene sediments have much less organic N and uniformly moderate concentrations of dissolved NH_4^+ . Though it is possible that NH_4^+ was produced throughout the anoxic parts of the

flow system, it is considered likely that most of the NH_4^+ in the deeper saline ground waters was produced near the sediment-water interface and carried downward with the water. NH_4^+ was also abundant in some of the fresh pore waters squeezed from sediment cores near the upper boundary of the freshwater plume, possibly indicating recharge in coastal freshwater wetlands or relatively reducing conditions in the uppermost parts of the aquifer. More detailed study of the distributions and isotopic compositions of coexisting organic N and NH_4^+ in the shallow parts of the flow system could provide more definitive evidence on these issues.

Patterns of Ground-Water Flow

Despite uncertainties in the interpretation of the age results, it may be concluded that both the fresh and saline pumped subestuarine ground waters were recharged mainly within the last 50 years. The freshwater beneath the Bay can be considered as a continuation of the surficial aquifer with sources of water and nitrate beneath the upgradient land surface (fig. 11). Like surficial aquifers on land, the fresh subestuarine ground-water plume appears to be stratified, with deeper waters having relatively old recharge dates and distant recharge areas. The apparent ages of the fresh subestuarine ground-water samples are similar to or slightly older than those of ground waters at comparable depths in surficial aquifers beneath the Delmarva Coastal Plain.

Although these data indicate that fresh ground water beneath the estuary at least 300 m from shore is part of an active flow system, they do not indicate directly the pattern or rate of fresh ground-water discharge to the bottom of the estuary. It is possible that fresh ground-water discharge occurs offshore in focused discharge areas (springs) that were not intercepted by the geophysical or coring operation, or that discharge is preceded by thorough mixing with saline ground water below the sediment-water interface. McKenna and others (2001) reported thermal features in Rehoboth and Indian River Bays that may include areas of rapid focused discharge. Additional work on this issue could be important because of the different effects these modes of discharge might have on nutrient

transport. The organic-rich Holocene sediments are considered to represent a potential biogeochemical barrier to slow, pervasive movement of NO_3^- into the estuary from below, but perhaps not to rapid, focused discharge of NO_3^- . The distribution of younger fresh ground waters (0 to 20 years old) in the discharge area would be especially relevant because of their higher potential NO_3^- concentrations (Böhlke and Denver, 1995) and faster potential discharge rates.

One of the most interesting results of this study is that the deep saline ground waters at locations WN1 and WN2 appear to be relatively young. According to the ^3H - ^3He data, the apparent ages of the deep saline samples increase offshore, and in WN2, the deep saline water appears to be younger than the overlying freshwater. If these tentative age interpretations are even qualitatively correct, they would imply relatively rapid downward movement of saline water around the edges of the freshwater plume, with the youngest deep ground-water ages (as at site WN1) perhaps indicating areas of preferential downwelling. At site WN1-71, the apparent age (2.2 years) and depth (21.6 m) of the saline ground water yield an apparent downward net vertical component of velocity of approximately 10 m/year. For an estimated porosity of 40 percent, this would correspond to a net local subestuarine recharge rate of 4 m/year. However, these data do not address the magnitudes of water and chemical fluxes near the sediment-water interface and over short time scales, which could include flow reversals caused by changes in surface-water levels as a result of tides and winds. Upward diffusion or advection of NH_4^+ formed by degradation of organic matter in the Holocene sediments could be a substantial source of N to the overlying estuary.

SUMMARY AND CONCLUSIONS

Stable isotopes and other environmental tracers were analyzed in samples of subestuarine ground water beneath Indian River Bay, Delaware to determine patterns of flow and sources and fate of nitrogen. These analyses were done through a cooperative agreement between the U.S. Geological Survey and the Delaware Department of Natural Resources and Environmental Control as part of a larger study

of ground-water discharge and nutrient enrichment in coastal estuaries.

Geophysical studies indicated freshwater plumes beneath the estuary at depths between 0 and 30 meters and extending at least 500 to 1,000 meters offshore. Analyses of ground-water samples from 3 to 22 meters beneath the bay confirmed the geophysical results, indicating that freshwater plumes were bounded by saline water with salinity similar to the estuarine surface water. Though the pumped ground-water sample set was small, and some of the analyses yielded complicated results, the isotopes and environmental tracer data from the vicinity of a plume north of White Neck, Delaware, indicate the following:

- (1) Much of the ground water beneath the estuary was recharged within the last 50 years. This includes both fresh and saline endmembers at depths ranging to at least 22 meters below the sediment-water interface.
- (2) The fresh ground-water plume to at least 300 meters offshore beneath the estuary is an actively flowing continuation of the surficial aquifer with recharge areas on land.
- (3) Nitrate transported offshore in the fresh ground-water plume was formed in aerated soils in agricultural or mixed land-use areas.
- (4) Denitrification occurred in the upper part of the aquifer where nitrate-bearing fresh ground water encountered reducing conditions within the aquifer.
- (5) Saline ground water was recharged from the estuary and moved downward relatively rapidly around the freshwater plume.
- (6) Ammonium transported downward in saline ground water was formed in anoxic to suboxic environments by degradation of organic matter in estuarine sediments.

Though it is evident that the subestuarine ground-water flow system is active and complex, these limited data do not provide evidence for discharge of fresh ground water in offshore areas of the estuary. Direct subestuarine discharge of fresh ground water containing nitrate that has not been denitrified is considered to be most likely near the shoreline or in offshore focused-discharge areas such as springs, which were not sampled in this study. Ammonium produced by degradation of organic matter in subestuarine sediments may be a substantial source of fixed nitrogen near the

sediment-water interface in much of the offshore area of the estuary.

This study establishes two general features of the subestuarine ground water that could guide future studies: (1) anthropogenic atmospheric environmental tracers including tritium (and decay-product helium), chlorofluorocarbons, and sulfur hexafluoride are appropriate dating tools for the time scale of interest, but multi-component analyses may be required to establish the reliability of derived ages; and (2) the speciation of nitrogen at depth is complex and spatially variable, so that multi-component chemical and isotopic analyses are required to resolve nitrogen sources and transformations. More complete information about the vertical and lateral gradients in ground-water ages of the freshwater plumes, especially along their upper boundaries, might yield more information about the distribution of freshwater discharge. Confirmation of the apparent pattern of rapid saline ground-water movement around the plumes could be especially valuable for testing complex variable-density models of subestuarine flow. More detailed analysis of the boundaries between freshwater plumes and surrounding saline ground waters might yield new information about relations between ammonium and nitrate and the distribution of denitrification beneath Indian River Bay and other similar subestuarine environments.

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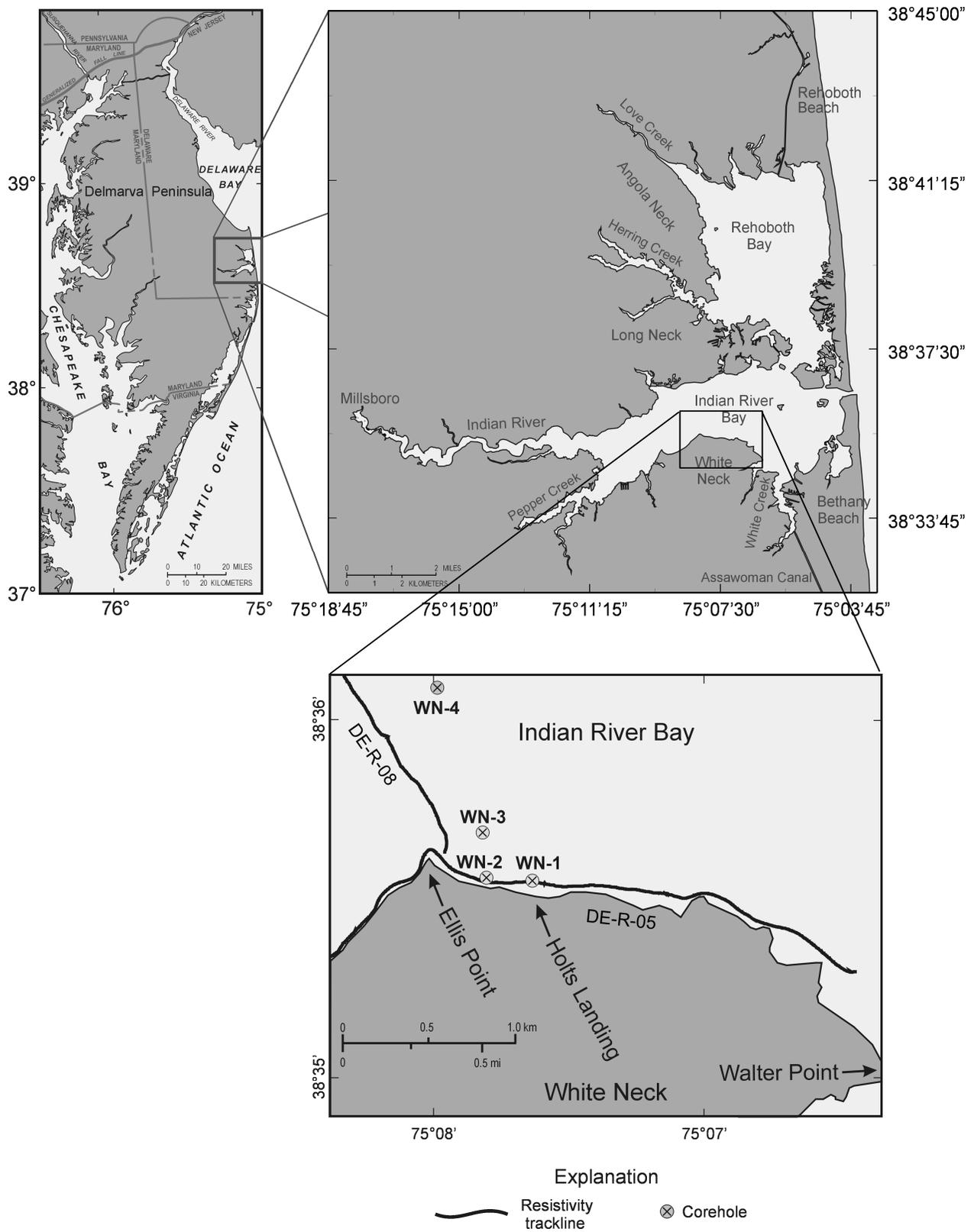


Figure 1. Ground-water sampling sites (WN-1 to WN-4) and resistivity survey tracklines (DE-R-05 and DE-R-08) in Indian River Bay near White Neck, Delaware (modified from Krantz and others, in press).

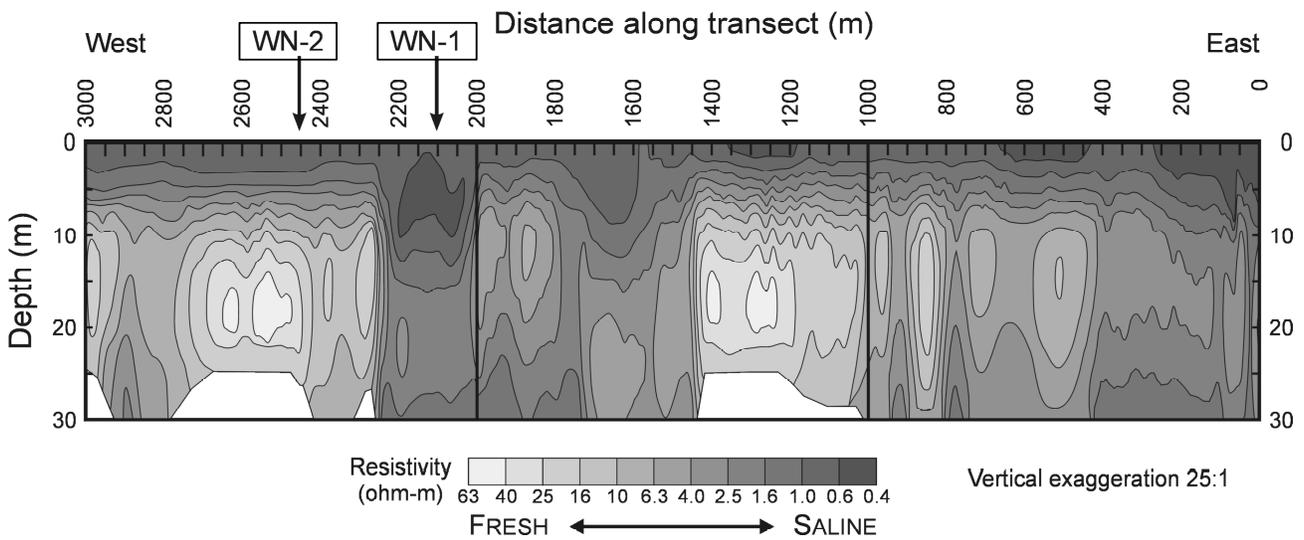
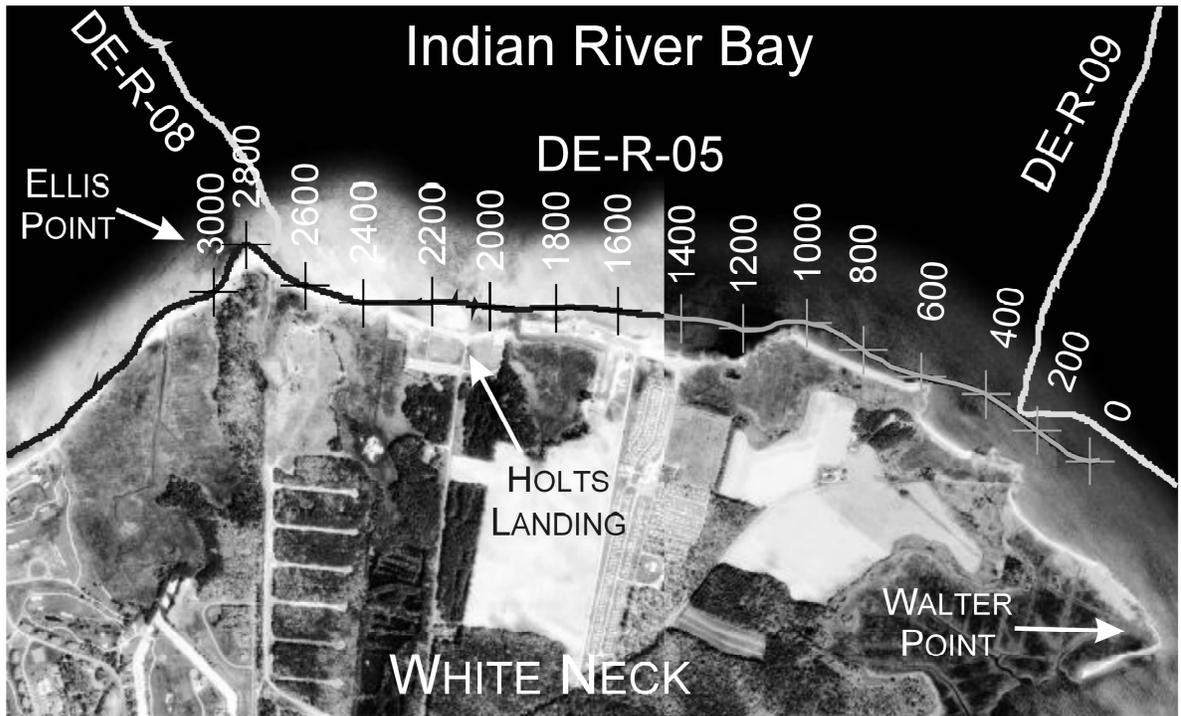


Figure 2. Streaming resistivity section DE-R-05 from Indian River Bay near White Neck, Delaware (modified from Krantz and others, in press) [m = meters; ohm-m = ohm-meters]. Approximate locations of ground-water sampling sites WN-1 (little or no freshwater) and WN-2 (thick freshwater plume) are shown on the resistivity section.

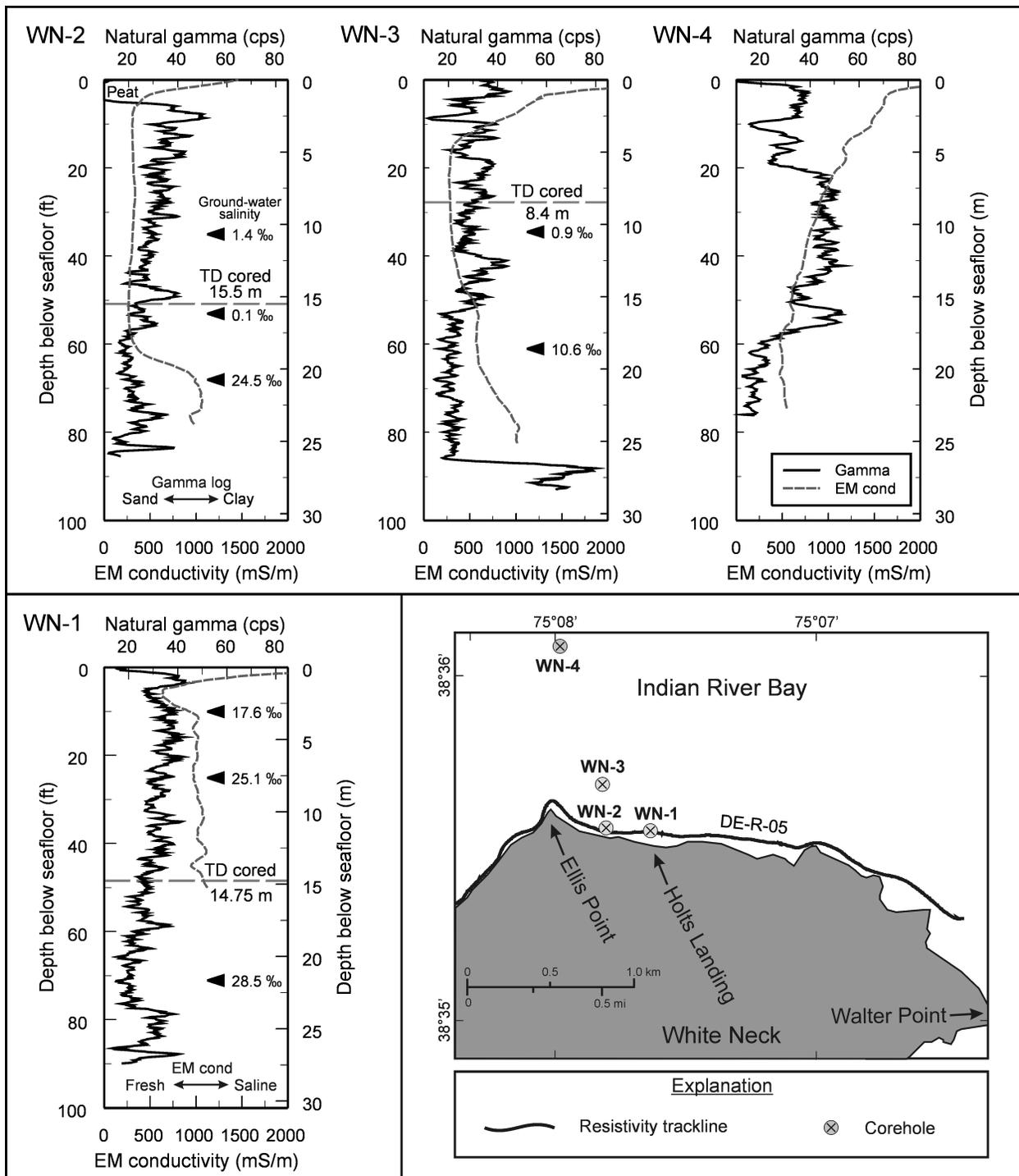


Figure 3. Site map and vertical profiles showing the distribution of pumped ground-water samples and geophysical logs (modified from Bratton and others, in press; Krantz and others, in press) [depths in ft (feet) and m (meters)]. The site map includes resistivity trackline DE-R-05 and the corehole sites WN-1 to WN-4. Vertical profiles include natural gamma logs (cps = counts per second; low in sand and high in clay) and electromagnetic induction (EM) conductivity logs (mS/m = millisiemens per meter; low in freshwater and high in saline water). Measured salinities (in ‰, or grams per kilogram) of pumped ground-water samples are shown in the profiles for comparison with the geophysical data. “TD cored” indicates the total depth of the cored sediments at sites WN-1, WN-2, and WN-3.

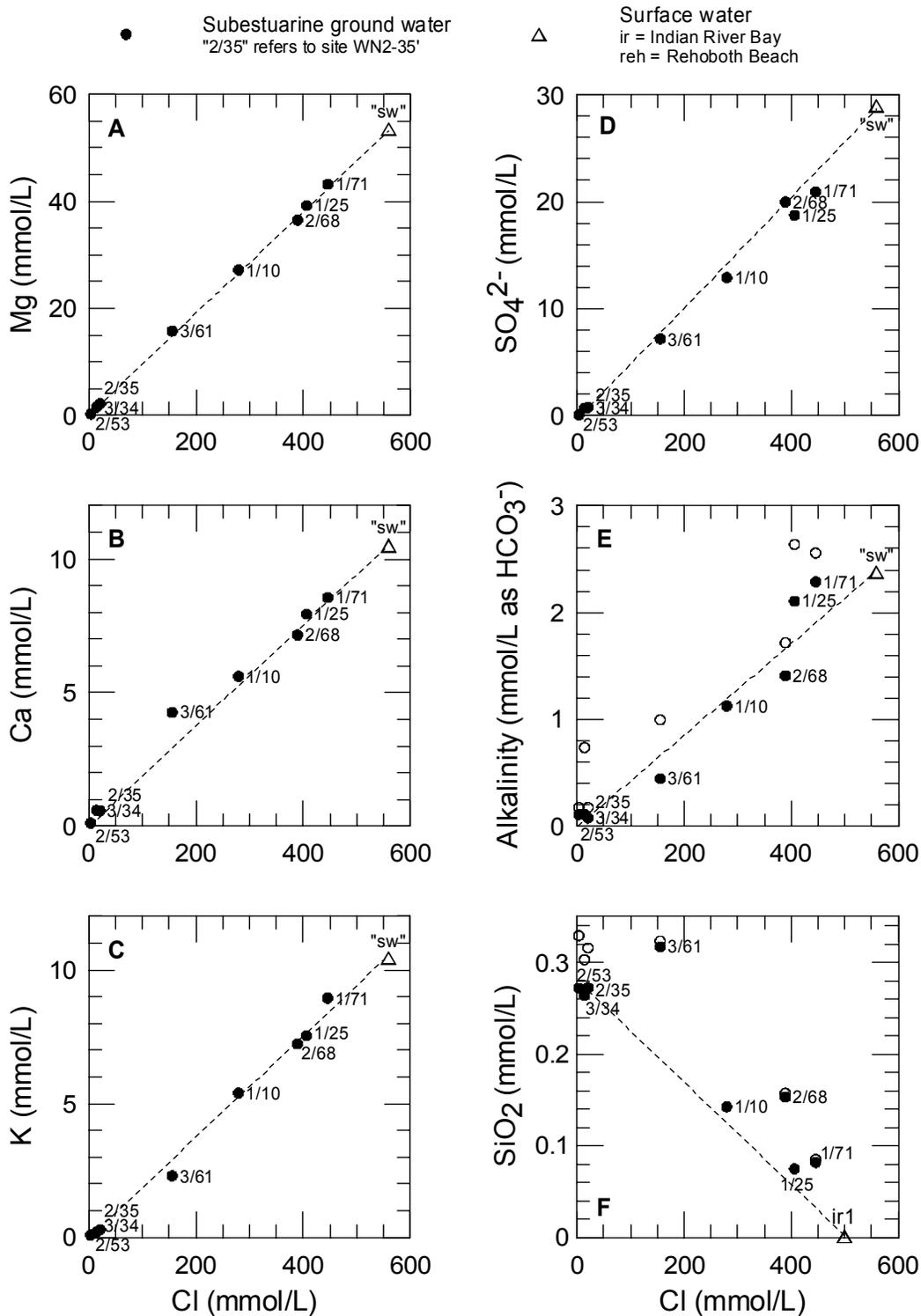


Figure 4. Relations between chloride and other major ions. [A] magnesium (Mg) and chloride (Cl⁻); [B] calcium (Ca) and Cl⁻; [C] potassium (K) and Cl⁻; [D] sulfate (SO₄²⁻) and Cl⁻; [E] alkalinity (as HCO₃⁻ or bicarbonate equivalents) and Cl⁻; [F] silica (SiO₂) and Cl⁻ [data from table 1; mmol/L = millimole per liter]. Closed symbols indicate laboratory analyses from the Reston water chemistry laboratory (RWCL in table 1); open symbols in [E] indicate field alkalinity analyses; open symbols in [F] indicate laboratory SiO₂ analyses from the University of Delaware (UDEL in table 1). The label "sw" refers to standard mid-ocean seawater, "ir1" indicates Indian River bay water, and the pumped ground-water samples are identified by site and depth in feet (for example 2/35 is from site WN-2, 35 feet below the sediment-water interface) (see table 1).

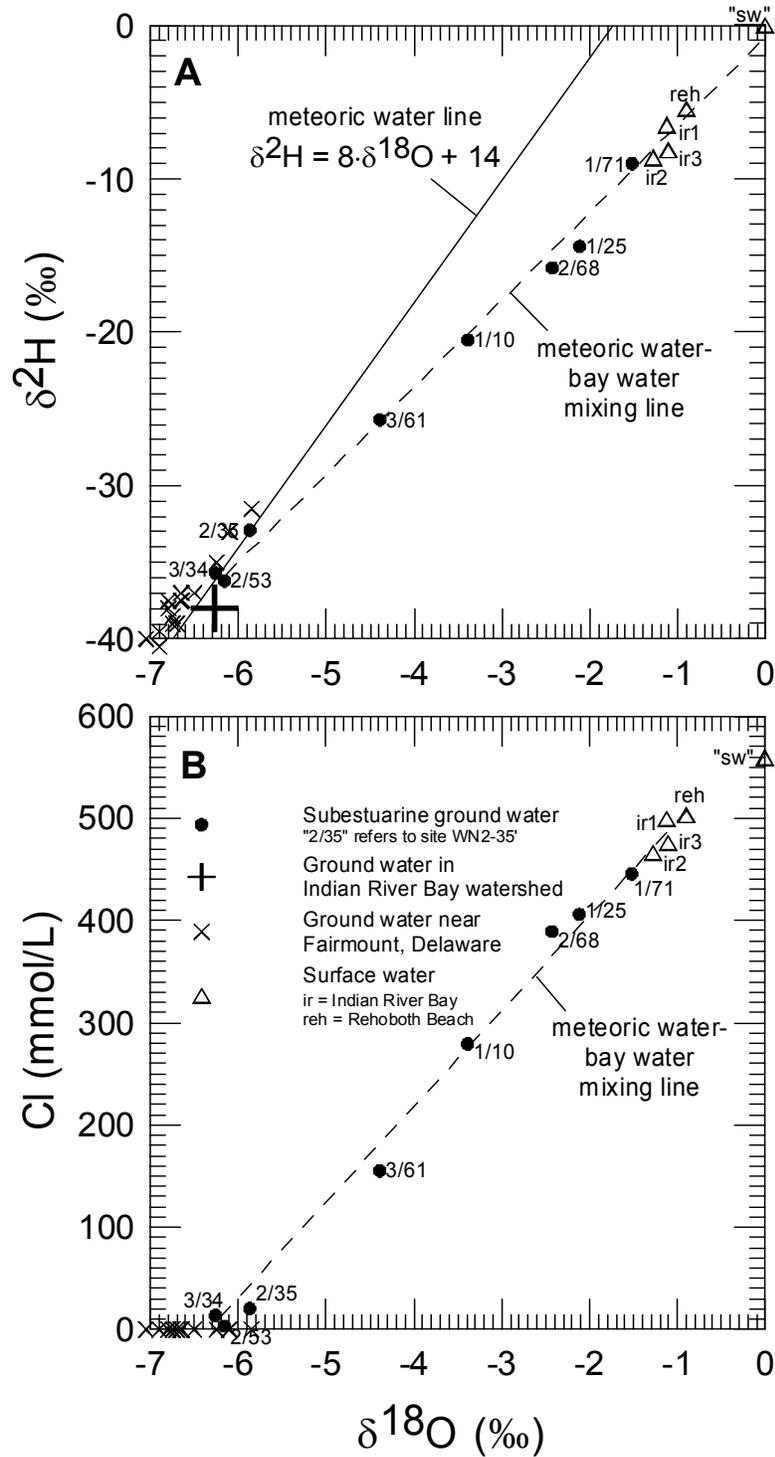


Figure 5. Comparison of $\delta^2\text{H}$, $\delta^{18}\text{O}$, and chloride concentrations. [A] $\delta^2\text{H}$ and $\delta^{18}\text{O}$; [B] chloride (Cl^-) and $\delta^{18}\text{O}$ [data from table 1; ‰ = per mil; mmol/L = millimole per liter]. The explanation in [B] applies to both panels. Landward ground-water data are included for areas near Indian River Bay (Andres, 1991; Dunkle and others, 1993). The label "sw" refers to standard mid-ocean seawater, "ir1" to "ir3" indicate Indian River bay samples, "reh" indicates ocean water from Rehoboth Beach, and the pumped ground-water samples are identified by site and depth in feet (for example 2/35 is from site WN-2, 35 feet below the sediment-water interface) (see table 1).

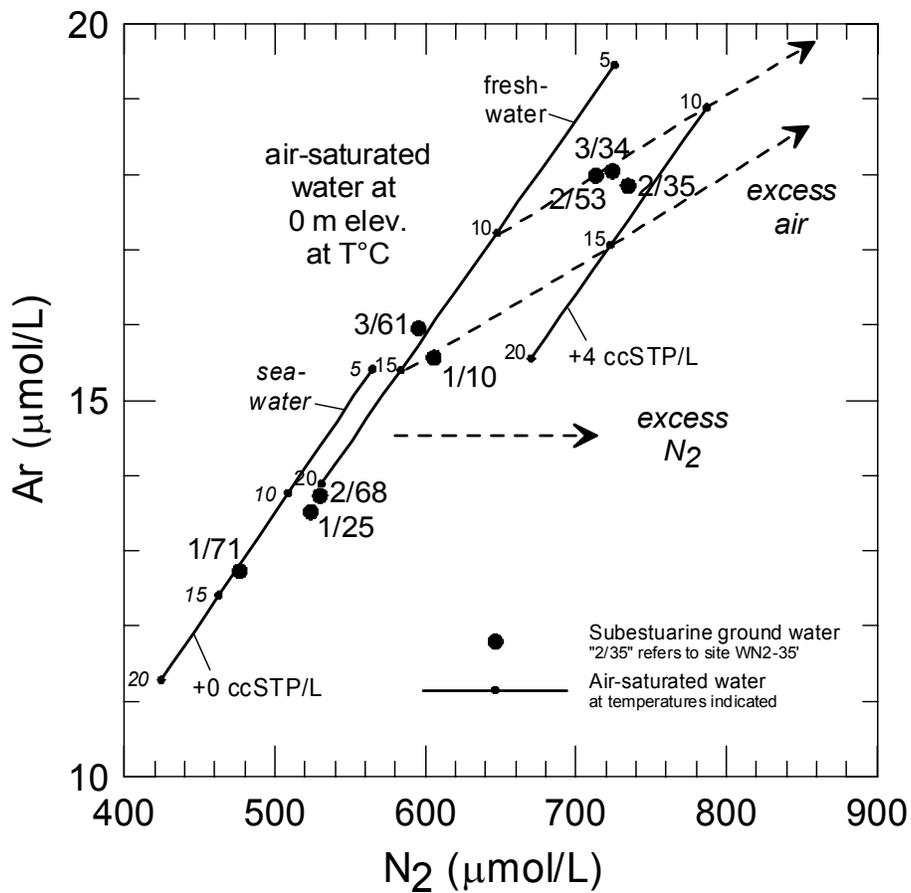


Figure 6. Concentrations of Ar (argon) and N₂ (nitrogen) in pumped ground-water samples [$\mu\text{mol/L}$ = micromoles per liter]. Air-saturation curves were calculated using solubilities from Weiss (1970) assuming elevation = 0 meters, salinity = 0 (freshwater) and 35 grams per kilogram (seawater), $\text{air}_{\text{excess}} = 0$ and +4 ccSTP/L (cubic centimeters of gas, at standard temperature and pressure, per liter), and temperature = 5 to 20 °C (degrees Celsius). The pumped ground-water samples are identified by site and depth in feet (for example 2/35 is from site WN-2, 35 feet below the sediment-water interface) (see table 1).

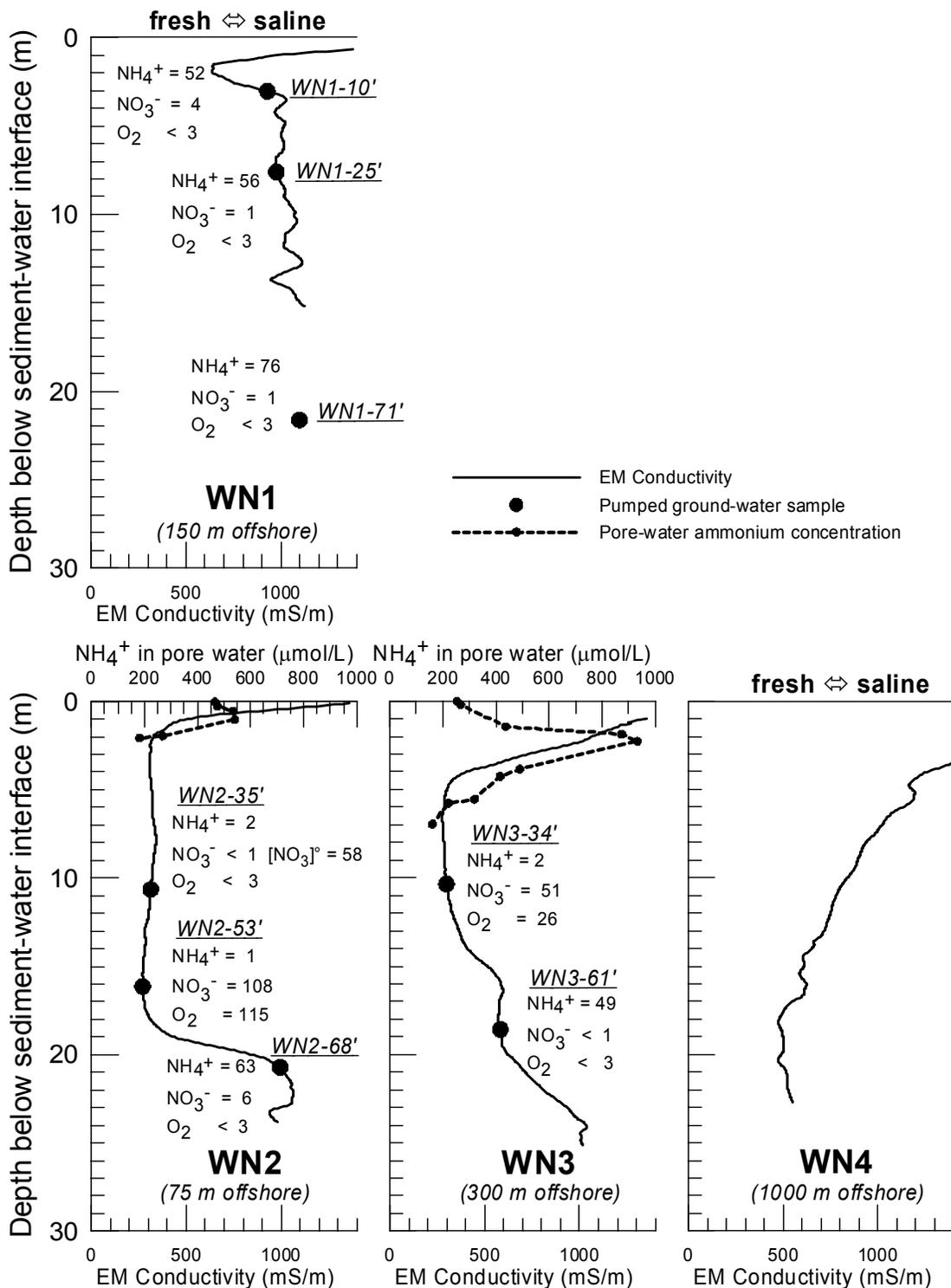


Figure 7. Vertical profiles showing the concentrations of NH_4^+ (ammonium), NO_3^- (nitrate), $[\text{NO}_3^-]^\circ$ (initial nitrate), and O_2 (oxygen) in pumped ground-water samples. The pumped samples are plotted at the sample depths (m = meters) in relation to the measured or interpolated values of electromagnetic induction (EM) conductivity given in mS/m (millisiemens per meter) from the geophysical logs (solid curves; see fig. 3). Dashed curves indicate concentrations of NH_4^+ in pore waters squeezed from shallow sediment cores at sites WN2 and WN3 (pore-water data from Bratton and others, in press).

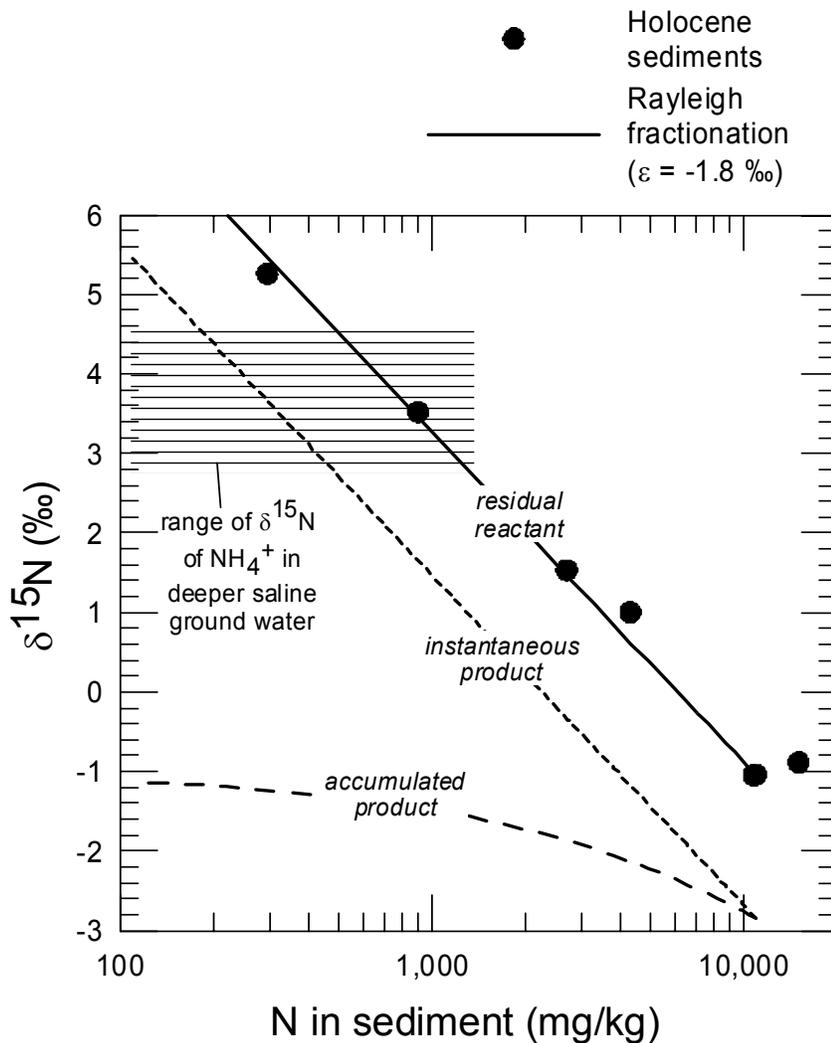


Figure 8. Nitrogen concentrations and $\delta^{15}\text{N}$ values of Holocene sediment samples (data from table 2), with hypothetical isotope fractionation curves for reactant (solid curve) and product (dashed curves) [mg/kg = milligrams per kilogram in sediment; ‰ = per mil]. The range of $\delta^{15}\text{N}$ values of dissolved NH_4^+ in deeper saline ground waters (table 1, minus 1 outlier) is shown for comparison. The apparent isotope fractionation factor ϵ for N loss from the sediments is defined by $\epsilon = (\alpha - 1) \cdot 1000 \text{ ‰}$, where $\alpha = \frac{[^{15}\text{N}/^{14}\text{N}]_{\text{product}}}{[^{15}\text{N}/^{14}\text{N}]_{\text{reactant}}}$ (see also equation 6).

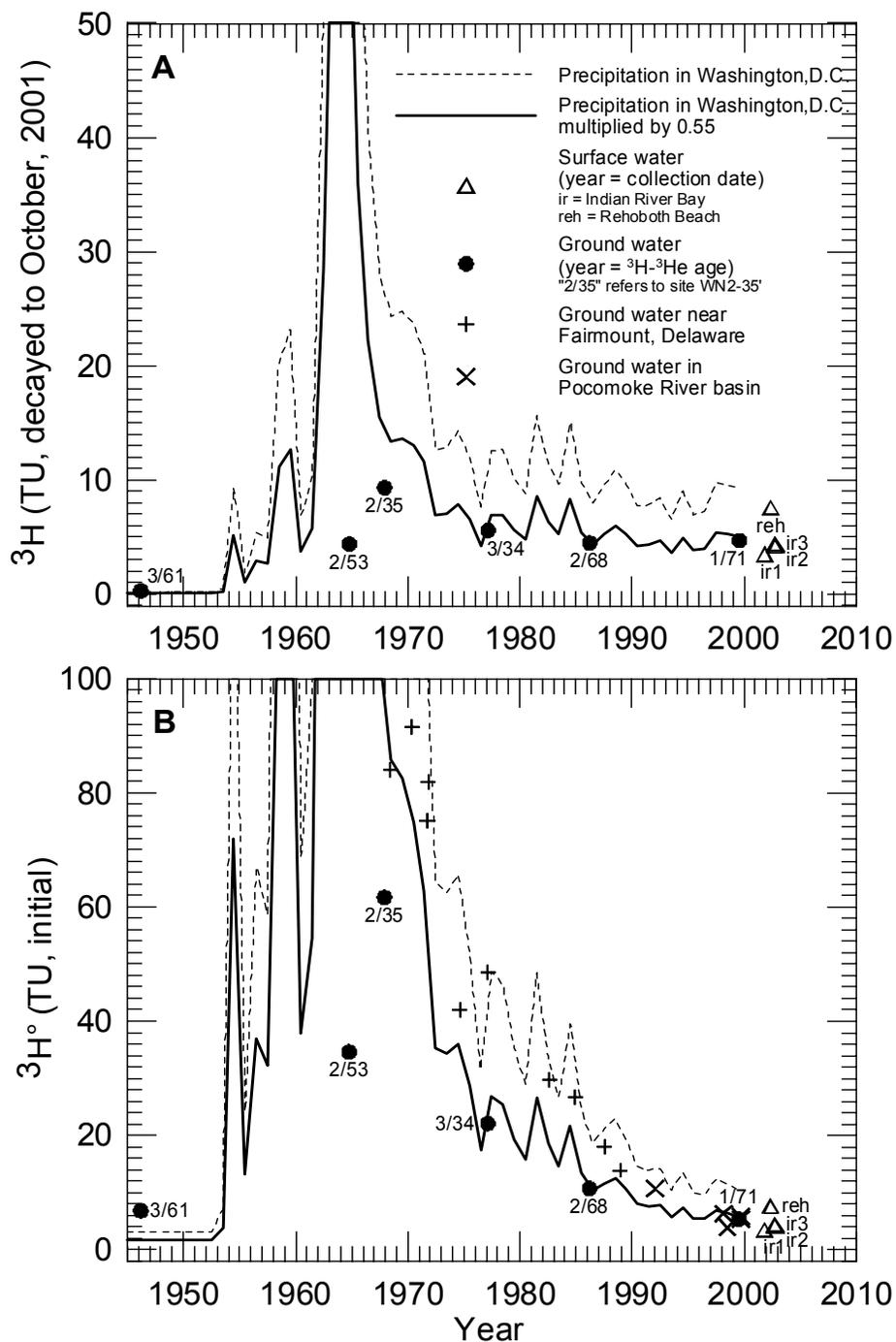


Figure 9. Documented and inferred records of ^3H (tritium) concentrations in precipitation and recharging ground water, compared with measured and calculated values for subestuarine ground-water samples from Indian River Bay, Delaware (table 1) [TU = tritium units]. The pumped ground-water samples are identified by site and depth in feet (for example 2/35 is from site WN-2, 35 feet below the sediment-water interface) (see Table 1). Shown for comparison are data for Washington, D.C. (IAEA, 1999, R.L. Michel, USGS, written commun., 2002). The hypothetical curve for the Delaware coast was drawn by assuming it was correlated with the Washington, D.C. curve but systematically lower (multiplied by 0.55). [A] ^3H values as measured at the time of sampling in October, 2001 (after radioactive decay). [B] Initial (undecayed) values. The explanation in [A] applies to both panels. Additional ground-water data from Fairmount, Delaware, are from Ekwurzel and others (1994). Data from the Pocomoke River basin are from Lindsey and others (in press).

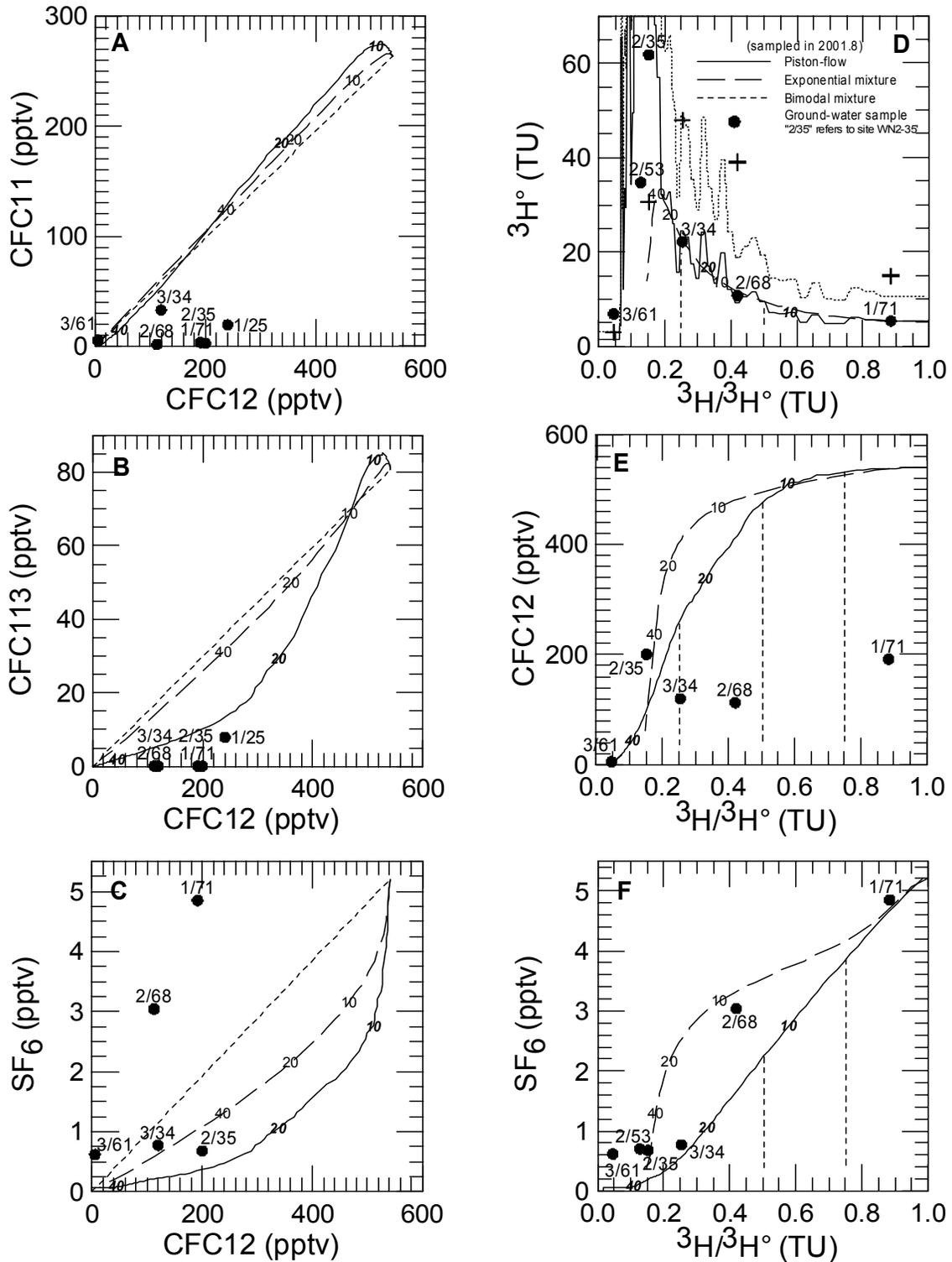


Figure 10. Comparison of environmental tracer data with hypothetical values. In each panel, the solid curve indicates concentrations and ratios of tracers that would yield concordant ages in the absence of mixing, contamination, or degradation (pptv = parts per trillion by volume of gas phase in equilibrium with the water sample; TU = tritium units). The long-dashed curve indicates concordance of mean ages for exponential mixtures (Cook and Böhlke, 2000; Böhlke, 2002). Short-dashed lines indicate concordance of binary mixtures in which one endmember is > 50 years old and contains no tracer. Curves are labeled with mean ages of hypothetical samples with representative concordant tracer concentrations. Light crosses in [D] indicate $^3\text{H}^0$ concentrations that would be required to explain the CFC12 deficits by mixing (see text and table 1, last column).

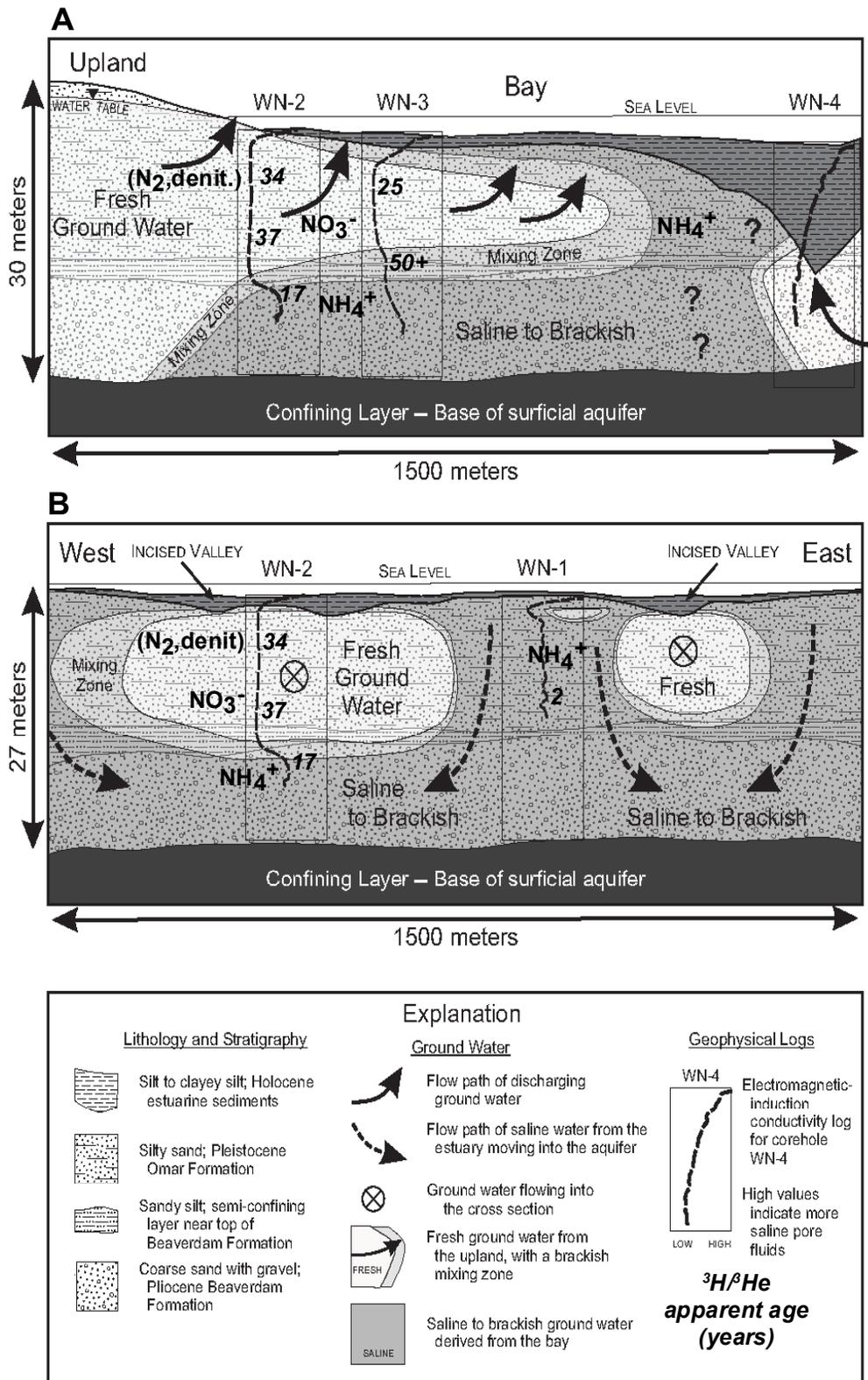


Figure 11. Schematic diagrams showing the distribution of fresh and saline ground water beneath Indian River Bay near White Neck, Delaware, with the distribution of ground-water ages (numbers in italics) and nitrogen species (NH₄⁺ = ammonium; NO₃⁻ = nitrate; N₂,denit = excess N₂ attributed to denitrification) (modified from Bratton and others, in press; Krantz and others, in press). [A] Section perpendicular to the shoreline. [B] Section parallel to the shoreline.

Table 1. Chemical and isotopic data for pumped ground waters and surface waters

[Units of measure are: m, meter; μm , micrometer; g, gram; mg, milligram; kg, kilogram; mmol, millimole; μmol , micromole; fmol, femtomole (10^{-15} mole); mS, millisiemen; μS , microsiemen; ccSTP, cubic centimeters of gas at standard temperature (0°C) and pressure (1 atmosphere); %, per mil (part per thousand); pptv, parts per trillion by volume, atmospheric mixing ratio of gas in equilibrium with a water sample; TU, tritium unit (1 atom of ^3H per 10^{18} atoms of ^1H). Chemical symbols are: O_2 , molecular oxygen; H_2O , water; Na, sodium; K, potassium; Mg, magnesium; Ca, calcium; Sr, strontium; Cl^- , chloride; NO_3^- , nitrate; SO_4^{2-} , sulfate; SiO_2 , silica; PO_4^{3-} , phosphate; CFC11, chlorofluorocarbon CCl_3F ; CFC12, chlorofluorocarbon CCl_2F_2 ; CFC113, chlorofluorocarbon $\text{C}_2\text{Cl}_3\text{F}_3$; SF_6 , sulfur hexafluoride; ^3H , tritium; He, helium; Ne, neon. Sources of data are: LDEO, Lamont-Doherty Earth Observatory (Noble Gas Laboratory); UDEL, University of Delaware at Lewes; MPTL, USGS Menlo Park Tritium Laboratory; NWQL, USGS National Water Quality Laboratory; RCFC, USGS Reston Chlorofluorocarbon Laboratory; RWCL, USGS Reston Water Chemistry Laboratory; RSIL, USGS Reston Stable Isotope Laboratory. "Select" indicates values that represent either averages or choices based on critical evaluation; shaded entries have relatively large uncertainties]

Annotations:

- [1] Samples are identified by the corehole site, followed by the depth of the well screen beneath the sediment-water interface in feet.
- [2] BLS, "below land surface" (below the sediment-water interface)
- [3] Fit, Cl^- concentrations calculated from specific conductance data based on a regression with available titration Cl^- values
- [4] X, fraction of young water in a binary mixture required to account for ^3H , $^3\text{H}/^3\text{H}^\circ$, and CFC12 data if CFC12 is not degraded; one component of the mixture is tracer-free (pre-1940) and the other component has its age determined by the $^3\text{H}/^3\text{H}^\circ$ ratio.
- [5] Standard seawater composition from Stumm and Morgan (1996)

Table 1. Chemical and isotopic data for pumped ground waters and surface waters (continued)

Sample site [1]	Figure labels	Sample date	Field sample comments	Screen depth BLS (m) [2]	Log EM conduct. (mS/m)	Field pH (std. units)	Field O ₂ meter (mg/L)	Field O ₂ titration as CaCO ₃ (mg/L)	Field Cl titration (mg/L)	Field Cl fit (mg/L) [3]	Field salinity calc. (g/L)	Select density calc. (kg/L)	Select salinity calc. (g/kg)	RSIL H ₂ O δ ² H (‰)	RSIL H ₂ O δ ¹⁸ O (‰)
Ground water															
WN1-10'	1/10	10/24/2001	peristaltic pump, low yield yellowish mud drillpipe not cleaned	3.0	930	6.28	0.48	na	na	9,821	17.74	1.0107	17.56	-20.5	-3.39
WN1-25'	1/25	10/25/2001	Bennett pump, low yield drillpipe not cleaned	7.6	978	7.06	0.53	na	na	14,132	25.53	1.0167	25.11	-14.4	-2.12
WN1-71'	1/71	10/25/2001	Bennett pump, high yield Fe oxide in ³ H bottle	21.6	na	7.66	0.10	na	na	16,080	29.05	1.0194	28.50	-9.0	-1.52
WN2-35'	2/35	10/27/2001	Bennett pump, high yield	10.7	313	5.34	0.07	na	8.9	771	1.39	0.9981	1.40	-32.9	-5.87
WN2-53'	2/53	10/27/2001	Bennett pump, high yield	16.2	270	5.52	3.20	3.6	8.9	112	48	0.9971	0.09	-36.2	-6.16
WN2-68'	2/68	10/27/2001	Bennett pump, high yield	20.7	996	6.24	0.28	na	86.0	13,750	24.84	1.0161	24.45	-15.8	-2.43
WN3-34'	3/34	10/29/2001	Bennett pump, high yield Fe oxide in ³ H bottle	10.4	299	5.44	1.72	na	37.0	510	0.96	0.9977	0.96	-35.7	-6.26
WN3-61'	3/61	10/29/2001	peristaltic pump, bubbles mud in serum bottles Fe oxide in ³ H bottle	18.6	583	5.40	0.15	na	50.0	5,890	10.61	1.0052	10.56	-25.7	-4.39
Surface Water															
Indian River Bay ir1		10/24/2001	from Holts Landing								31.92	(lab) 1.0216	(lab) 31.25	-6.4	-1.15
Indian River Bay irb		10/26/2001	from Holts Landing								29.72	1.0199	29.14	-8.6	-1.28
Indian River Bay ir2		9/23/2002	from Holts Landing								30.38	1.0204	29.77	-8.1	-1.11
Indian River Bay ir3		9/25/2002	from Holts Landing								32.14	1.0217	31.46	-5.5	-0.91
Rehoboth Beach reh		5/12/2002													
sid seawater "sw"											35.86	1.0246	35.00	0.0	0.00

Table 1. Chemical and isotopic data for pumped ground waters and surface waters (continued)

Sample site [1]	RWCL Na (mmol/L)	RWCL K (mmol/L)	RWCL Mg (mmol/L)	RWCL Ca (mmol/L)	RWCL Sr (mmol/L)	RWCL Fe (mmol/L)	RWCL Mn (mmol/L)	RWCL SiO ₂ (mmol/L)	RWCL B (mmol/L)	RWCL Br (mmol/L)	RWCL Cl (mmol/L)	Field Cl (mmol/L)	RWCL SO ₄ ²⁻ (mmol/L)	RWCL NO ₃ ⁻ (mmol/L)	RWCL alkalinity as HCO ₃ ⁻ (mmol/L)	Field alkalinity (mmol/L)	RWCL Si (μmol/L)	UDEL Si (μmol/L)	UDEL PO ₄ ³⁻ (μmol/L)	UDEL NH ₄ ⁺ (μmol/L)	UDEL δ ¹⁵ N (‰)	UDEL NH ₄ ⁺ NO ₂₊₃ ⁻ (μmol/L)	UDEL NO ₂₊₃ ⁻ NO ₃ ⁻ (μmol/L)	RSIL L	RSIL L			
Ground water																												
WN1-10'	223	5.40	27.20	5.61	0.05	0.04	-0.01	0.14	0.21	0.41	279	277	12.91	<0.3	1.13	na	142	158	0.9	51.6	na	na	4.5	na				
WN1-25'	324	7.55	39.21	7.93	0.07	0.01	-0.01	0.07	0.31	0.63	406	399	18.74	<0.3	2.11	2.64	75	77	0.5	56.5	4.5	na	0.9	na				
WN1-71'	367	8.95	43.20	8.56	0.07	0.03	-0.01	0.08	0.35	0.69	446	454	20.92	<0.3	2.29	2.56	82	85	1.4	76.1	3.6	1.1	na	na				
WN2-35'	16	0.29	2.17	0.58	0.01	0.02	0.00	0.27	0.00	0.03	20	22	0.78	<0.02	0.08	0.18	272	316	0.6	2.5	na	0.6	na	0.6	na			
WN2-53'	3	0.08	0.24	0.13	0.00	0.01	0.00	0.27	0.00	0.01	3	1	0.07	0.11	0.11	0.18	272	329	0.6	0.9	na	108.1	105					
WN2-68'	304	7.24	36.49	7.16	0.06	0.00	-0.01	0.15	0.28	0.60	389	388	19.99	<0.8	1.41	1.72	153	157	0.6	63.4	13.0	5.8	na	na				
WN3-34'	11	0.19	1.56	0.61	0.01	0.02	0.00	0.26	0.00	0.02	14	15	0.71	<0.06	0.11	0.74	264	303	0.5	2.3	na	50.8	40					
WN3-61'	122	2.30	15.76	4.27	0.03	0.03	0.05	0.32	0.05	0.25	155	166	7.18	<0.2	0.45	1.00	317	323	0.7	49.2	2.8	0.4	na	na				
Surface Water																												
Indian River Bay	(calc)																											
Indian River Bay	500																											
Indian River Bay	466																											
Indian River Bay	476																											
Rehoboth Beach	503																											
<i>std seawater</i>	480	10.46	53.57	10.51	0.09				0.42	0.87	560	560	28.96		2.38	2.38												

[5]

Table 1. Chemical and isotopic data for pumped ground waters and surface waters (continued)

Sample site [1]	RWLRWCLRWCRLRWCRLRWCRLRSIL		Field		Aver. Ar		Aver. N ₂		Aver. Ar/N ₂		Aver. δ ¹⁵ N		LDEO		LDEO		LDEO		LDEO		AF-N ₂		Ne-Ar		Ne-Ar-N ₂		Select	
	O ₂ (μmol/L)	CO ₂ (μmol/L)	CH ₄ (μmol/L)	O ₂ (L)	Ar (μmol/L)	CH ₄ (μmol/L)	Ar (L)	N ₂ (μmol/L)	N ₂ (L)	Ar/N ₂ (μmol/μmol)	N ₂ (L)	δ ¹⁵ N (‰)	δ ³ He (per-cent)	He (ccSTP/ g)	He (μmol/L)	Ne (ccSTP/ g)	Ne (μmol/L)	AF-N ₂ T (°C)	AF-N ₂ air excess (ccSTP/ L)	AF-N ₂ T (°C)	AF-N ₂ air excess (ccSTP/ L)	Ne-Ar T (°C)	Ne-Ar air excess (ccSTP/ L)	Ne-Ar-N ₂ T (°C)	Ne-Ar-N ₂ air excess (ccSTP/ L)	Select T (°C)	Select air excess (ccSTP/ L)	Select N ₂ excess (μmol/L)
Ground water																												
WN1-10'	2	0	0.32	16.16	635	2.55	0.99	15	2	0.33	15.57	606	2.57	0.96	na	na	na	11.1	1.3	na	na	na	na	na	na	11.1	1.3	<20
	2	0	0.34	14.98	577	2.60	0.93																					
WN1-25'	2	0	0.68	13.52	527	2.57	0.74	17	2	0.70	13.52	524	2.58	0.79	na	na	na	15.2	0.9	na	na	na	na	na	15.2	0.9	<20	
	2	0	0.71	13.51	521	2.59	0.84																					
WN1-71'	2	0	0.61	12.77	477	2.68	0.84	3	1	0.61	12.73	477	2.67	0.86	0.9	4.03	0.0018	16.72	0.00761	15.7	0.0	16.2	0.3	-6	16.0	0.2	<10	
	1	0	0.61	12.70	476	2.67	0.88							1.2	4.03	0.0018	16.52	0.00752			16.0	0.2	-4					
WN2-35'	2	0	0.00	17.78	732	2.43	1.02	2	2	0.00	17.85	735	2.43	1.06	173.5	5.37	0.0024	23.39	0.01042	11.5	3.3	10.0	1.8	29	10.0	1.8	29	
	2	0	0.00	17.92	737	2.43	1.09																					
WN2-53'	116	0	0.07	18.01	715	2.52	0.64	100	115	0.04	17.99	713	2.52	0.61	93.3	5.74	0.0026	24.39	0.01086	10.1	1.9	10.5	2.4	-8	10.3	2.2	<10	
	115	0	0.00	17.96	712	2.52	0.57																					
WN2-68'	2	0	0.52	13.72	530	2.59	0.60	9	2	0.54	13.73	530	2.59	0.65	22.9	4.47	0.0020	18.23	0.00827	14.5	0.8	14.4	0.8	1	14.5	0.8	<10	
	2	0	0.56	13.75	530	2.60	0.70																					
WN3-34'	28	0	0.00	18.15	731	2.48	0.71	54	26	0.00	18.05	724	2.49	0.71	73.3	2.43	0.0011	11.73	0.00523	10.2	2.4	3.1	-5.4	159	10.2	2.4	<20	
	24	0	0.00	17.94	717	2.50	0.71							73.2	3.95	0.0018	17.58	0.00783			6.1	-1.8	86					
<i>He-Ne samples partially degassed?</i>																												
WN3-61'	1	0	0.50	15.86	588	2.70	na	5	1	0.51	15.96	595	2.68	0.93	-13.1	7.11	0.0032	21.27	0.00955	10.3	-0.1	12.2	1.5	-32	10.3	-0.1	<20	
	1	0	0.51	16.06	602	2.66	0.93																					
Surface Water																												
Indian River Bay																												
Indian River Bay																												
Indian River Bay																												
Indian River Bay																												
Rehoboth Beach																												
<i>std seawater</i>																												
/5/																												

Table 1. Chemical and isotopic data for pumped ground waters and surface waters (continued)

Sample site [1]	RCFC SF ₆ (fmol/L)		RCFC SF ₆ Aver. (pptv)		σ SF ₆ (pptv)		RCFC SF ₆ recharge date (years)		RCFC SF ₆ recharge age (years)		RCFC SF ₆ recharge date (years)		RCFC SF ₆ recharge age (years)											
	RCFC SF ₆ (fmol/L)	RCFC SF ₆ Aver. (pptv)	σ SF ₆ (pptv)	RCFC SF ₆ recharge date (years)	RCFC SF ₆ recharge age (years)	RCFC SF ₆ recharge date (years)	RCFC SF ₆ recharge age (years)	RCFC SF ₆ (fmol/L)	RCFC SF ₆ Aver. (pptv)	σ SF ₆ (pptv)	RCFC SF ₆ recharge date (years)	RCFC SF ₆ recharge age (years)	RCFC SF ₆ (fmol/L)	RCFC SF ₆ Aver. (pptv)	σ SF ₆ (pptv)									
Ground water																								
WNI-10'	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na									
WNI-25'	2.67 2.78 9.07	8.71	8.89	0.25	contaminated?	122 299 287	9.7 23.9 23.0	18.9	8.0	1963	39	na	809 803 811	237.8 235.9 238.5	1.3	1976	26	0 41 48	0.0 10.7 12.5	7.7	6.8	1972	30	
WNI-71'	1.34 1.34	4.84 4.85	4.85	0.01	2000	2 39	2.2 3.4	2.8	0.8	1954	48	na	602 601	190.7 190.4	0.2	1974	28	0 0	0.0 0.0	0.0	0.0	<1955	>46	
WN2-35'	0.31 0.34	0.64 0.71	0.68	0.05	1979	23 55 25	2.4 2.6 1.2	2.1	0.8	1954	48	na	1059 1081 1056	195.6 199.8 195.1	2.6	1974	28	0 0 0	0.0 0.0 0.0	0.0	0.0	<1955	>46	
WN2-53'	0.34 0.36	0.68 0.72	0.70	0.03	1979	23 1694 1694	82.1 82.4 82.4	82.3	0.2	1973	29	na	7402 7466 7483	1367 1379 1382	7.9	contaminated?	?	0 0 0	0.0 0.0 0.0	0.0	0.0	<1955	>46	
WN2-68'	0.96 0.99	2.99 3.08	3.04	0.06	1993	9 15 13 12	1.1 1.0 0.9	1.0	0.1	1952	50	na	382 410 380	108.5 116.4 107.9	4.7	1969	33	0 0 0	0.0 0.0 0.0	0.0	0.0	<1955	>46	
WN3-34'	0.41 0.37	0.81 0.73	0.77	0.06	1980	22 663 655	32.3 32.0	32.2	0.2	1966	36	na	675 591	124.8 109.2	11.0	1970	32	0 0	0.0 0.0	0.0	0.0	<1955	>46	
WN3-61'	0.23 0.23	0.61 0.63	0.62	0.01	1978	24 136 67 64	7.3 3.6 3.4	4.8	2.2	1956	46	na	20 18 32	4.3 3.7 6.7	1.6	1949	53	1265 668 277	222.1 117.2 48.6	129	87.4	contaminated		
Surface Water																								
Indian River Bay																								
Indian River Bay																								
Indian River Bay																								
Indian River Bay																								
Rehoboth Beach																								
<i>std seawater</i>																								
[5]																								

Table 2. Concentration and isotopic composition of nitrogen in sediments

[mg/kg, milligrams per kilogram; ‰, per mil; na, not analyzed]

Corehole and depth below sediment-water interface, in feet	Sample depth (meters)	Sediment age	Nitrogen concentration (mg/kg)	Nitrogen $\delta^{15}\text{N}$ (‰)
WN1-6.0'	1.8	Pleistocene	12	na
WN1-8.6'	2.6	Pleistocene	11	na
WN1-10.8'	3.3	Pleistocene	12	na
WN1-17.2'	5.2	Pleistocene	12	na
WN1-19.1'	5.8	Pleistocene	10	na
WN1-24.0'	7.3	Pleistocene	13	na
WN1-27.2'	8.3	Pleistocene	10	na
WN1-33.1'	10.1	Pleistocene	11	na
WN1-43.0'	13.1	Pleistocene	12	na
WN2-6.5' (< 63 micron)	2.0	Holocene (?)	14,972	-0.89 (4.5 percent of sample)
WN2-6.5' (> 63 micron)	2.0	Holocene (?)	10,732	-1.05 (95.5 percent of sample)
WN2-6.5' (composite)			10,923	-1.04
WN3-0.6'	0.2	Holocene	296	5.3
WN3-2.0'	0.6	Holocene	59	na
WN3-3.5'	1.1	Holocene	901	3.5
WN3-9.1'	2.8	Holocene	4,319	1.0
WN3-11.0'	3.4	Holocene (?)	2,698	1.5
WN3-12.8'	3.9	Pleistocene	45	na
WN3-15.3'	4.7	Pleistocene	20	na
WN3-21.0'	6.4	Pleistocene	21	na
WN3-23.1'	7.0	Pleistocene	9	na

Table 3. Summary of ground-water age interpretations

[³H, tritium; ³H^o, initial tritium; He, helium; Ne, neon; CFC12, chlorofluorocarbon CCl₂F₂; SF₆, sulfur hexafluoride]

Sample name	Sample date	Age Summary (Apparent ³ H- ³ He ages are underlined)
WN1-10'	10/24/01	Age uncertain, could be 0-30 years from ³ H only
WN1-25'	10/25/01	Age uncertain, could be 0-30 years from ³ H and CFC12? SF ₆ contaminated, no He data
WN1-71'	10/25/01	About <u>2</u> years ³ H, ³ H- ³ He, and SF ₆ concordant CFC12 degraded?
WN2-35'	10/27/01	<u>28-34</u> years ³ H, ³ H- ³ He, and CFC12 roughly concordant SF ₆ close but slight background?
WN2-53'	10/27/01	<u>37-45?</u> years (late 1950s, early bomb, mixed?) low ³ H/ ³ H ^o , moderate ³ H ^o CFC12 contaminated, SF ₆ background?
WN2-68'	10/27/01	<u>9-16</u> years? ³ H, ³ H- ³ He, and SF ₆ poorly concordant CFC12 degraded?
WN3-34'	10/29/01	<u>22-25</u> years? ³ H, ³ H- ³ He, and SF ₆ concordant He+Ne degassed, CFC12 degraded?
WN3-61'	10/29/01	≥ 50 years (> 90 percent pre-bomb ³ H) undatable by these methods SF ₆ background?